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Potential threat of heavy metals and PAHs in PM2.5 in different urban functional areas of Beijing

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ABSTRACT

Beijing, as the capital of China, is one of the most populous cities in the world. With the fine particulate matter pollution being increasingly serious, daily exposure to hazardous ingredients caused more and more attention. Current research concerning risk evaluation in Beijing was relative less. In November, 2013, samples were collected in seven different functional areas of Beijing, so as to better understand the risk to human health caused by particle matter pollution in this region. PM2.5 pollution in rural and urban Beijing was relative high under haze–fog days in comparison with non haze–fog value. Zn and Ba showed the highest concentration levels among non-carcinogenic metals. The non-carcinogenic metal concentration at all the sites ranged in the same order: Ce, Pb, Cu, V and Sb. Higher ring PAHs (with four to six rings) were the dominant species and constituted more than 90% of the Σ_{14}PAHs. Pb (4.34×10^{-4} for men, 3.73×10^{-4} for women) presented the maximum risk level for non-carcinogenic heavy metals in the whole study area. While, risk levels of Cr at residential areas, schools, Olympic Park and rural countryside exceeded the limit for adults. In haze–fog days, the carcinogenic PAH risk level in each functional area ranged in the order: rural countryside > inner suburban district > Olympic Park > city central > schools > ecological reserve > residential areas. To some extent, benzo(a)pyrene may had a potential risk to adults, and other carcinogenic PAHs were all under average risk acceptance.

1. Introduction

As an international metropolis, Beijing air quality has been received more attention than other cities in China. Beijing had successfully hosted the Olympic Games in 2008. In particular, there still retain a large number of stadiums. Like many famous scenic spots, most stadiums were located in the north half area of Beijing, and attracted large numbers of tourists. At present, Beijing has successfully bid to host the 2022 winter Olympics. The air quality is directly related to the health of athletes and tourists. In recent years, the economic integration of the Beijing–Tianjin–Hebei region pattern prompted an expansion of the urban area in Beijing. As the result is the rapid expansion of population and vehicles, the problem of Beijing's air quality, especially, the fine particulate matter, has become the focus of attention, and more and more prominent. In order to effectively improve air quality, the government implemented a new National Ambient Air Quality Standard for PM2.5 (air dynamics equivalent diameter less than or equal to 2.5 μm, 75 μg m^{-3} for a 24 h average, level II; 35 μg m^{-3} for annual average, level II) (PRC National Standard, 2012). Measures devoted to air pollution control were determined by the State Council, including elimination of yellow cars, remediation on city raised dust and dining lampblack pollution. The Chinese government has made a statement that national air quality should be improved significantly in five years or longer. The Beijing–Tianjin–Hebei region fine particulate matter concentration should decrease by 25%, especially, the annual concentration of fine particulate matter of Beijing should be controlled within 60 μg m^{-3}. Earlier comprehensive study found the average concentration of PM2.5 at urban residential sites was in the 127 μg m^{-3} range more than a decade ago (Zheng et al., 2005). Since the 21st century, the average mass concentration of PM2.5 has increased significantly following rapid economic development in Beijing urban areas. What's more, recent study showed an average PM2.5 concentration of 115–150 μg m^{-3} during pollution episodes in urban Beijing (Song et al., 2015). These values were obviously higher than the levels found under the similar conditions in the United States and Europe. For example, the measured average concentration of PM2.5 in two sites of Pamplona (Spain) was only about 15.38 μg m^{-3} and 17.42 μg m^{-3} (Aldabe et al., 2011). A recent study showed that the average PM2.5 exposure was only about 15.8 μg m^{-3} for spring and 20.1 μg m^{-3} for fall in 12 municipalities of Mexico (Mancilla et al., 2015). A summary could be drawn from several studies that from

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2003 to 2013, the annual PM2.5 concentrations in Beijing ranged between 70 and 100 μg m^{-3} (Lang et al., 2013). Although the government's goals were clear, Beijing still experienced serious fine particulate matter pollution for some time.

PM2.5 has a great influence on atmospheric visibility and human health, and presents a more serious pollution in winter, China (Huang et al., 2007). Heavy metals and PAHs are important chemical compositions of PM2.5, and most elements present higher concentrations in winter. PM2.5 contains a large amount of harmful elements, especially toxic heavy metal elements which could do harm to the human body. Toxic heavy metals cause harm to the human body by exposure through three major ways: food intake, skin contact and inhalation (Dockery et al., 1992). Due to pollution caused by human activities, toxic heavy metals in the atmosphere are much higher than natural background value (Charlesworth et al., 2011). At present, domestic and international researches give priority to the PM2.5 source apportionment and potential ecological risk assessment. Research conducted in the zinc smelting district, northeast of China, manifested that Pb and Cd from street dust were detected as the most possible culprits to health risks (Zheng et al., 2010). As was the main carcinogenic heavy metal in the tropical region of Southeast Asia (Khan et al., 2016). The health risk evaluation was conducted in the majority with heavy metals in soil and water, and the ambient air, especially health risk assessment and the human exposure from heavy metals in atmospheric particles are less (Ferreira-Baptista and De Miguel, 2005; Díaz and Rosa Dominguez, 2009; Hu et al., 2012). PAHs were generated from incomplete combustion or pyrolysis of coal, oil and biomass (Mumford et al., 1987; Gong et al., 2012). In urban areas, traffic and industrial emissions were the predominant sources of PAHs (Y.N. Liu, et al., 2007; S. Liu et al., 2007; H. Shen et al., 2013; G. Shen et al., 2013; Zhang and Tao, 2009). In China, health risk evaluation was mainly conducted in serious polluted factory or mining areas. Research conducted in Taiyuan, China showed that the risk level of PAH pollution is significantly higher than the literature-reported national average level (Duan et al., 2014). Besides, researchers found that in Taiyuan, China, the median values of incremental life time cancer risk (ILCR) induced by whole year inhalation exposure for all groups were basically larger than 10^{-6}, with higher values in winter than in other seasons and in urban than in rural area (Xia et al., 2013).

In order to investigate the current situation of PM2.5 pollution in different functional areas of Beijing, a monitoring covering the northern half of Beijing was carried out in winter. The trace metal and PAH compositions were obtained. Chemical characteristics of PM2.5 were compared between different functional areas. At last, in order to provide theoretical basis for the local government, this study evaluated health risks of exposure to metals and PAHs in the levels observed in humans.

2. Material and methods

2.1. Sampling site

Beijing, which is considered as the economic and cultural center of China, has a permanent population of more than 20 million. Beijing lies in the north of the north China plain and belongs to the boundary of Yanshan Mountain, adjacent to Tianjin and Hebei province. As a famous tourist city, it attracts a large number of domestic and foreign tourists every year, and often hosts various international sports events. In order to study heavy metal and PAH exposure of human from particles, the northern half of Beijing, where numerous scenic spots, schools and stadiums were constructed, was chosen as study area. In this research, ambient PM2.5 samples were collected at different urban functional areas. Samples were collected at seven sites within concentric zones around Beijing, ranging from the second ring road to Miyun County, with a sampling site in each ring road (Fig. 1). Each sampling site lies in different urban functional areas. And these different areas include scenic spot, community, schools, parks/stadiums, villages, factories and ecological reserve (Table 1). Samples were collected in both haze and non-haze conditions according to the weather forecast issued by the weather bureau. Ecological reserve can be considered as background sampling site and there was no industrial activity surrounding.

2.2. Sampling methods

The PM2.5 samples were collected in 13 days during November 2013. All the samples were collected under no-rain weather conditions. In urban sampling process, human daily activities near sampling sites were normal as usual, and each sampling event lasted 24 h (from 8:00 a.m. to next 8:00 a.m.). In the sampling process, we used a median volume sampler along with PM2.5 cutting equipment (manufactured by Laoying, Qingdao, China) at a flow rate of 100 L min^{-1} to collect the samples, and the machine's flow recorder can compute each total volume automatically. All the samplers were placed 1.5 m above the ground. Glass fiber filters were used as sampling membrane (88 mm diameter, Beijing Synthetic Fiber Research Institute, Beijing, China). To remove volatile substances and other impurities, the membranes were baked at 450 °C for 12 h prior to sampling. The filters were weighed under controlled temperature and humidity conditions (25 °C, 50%

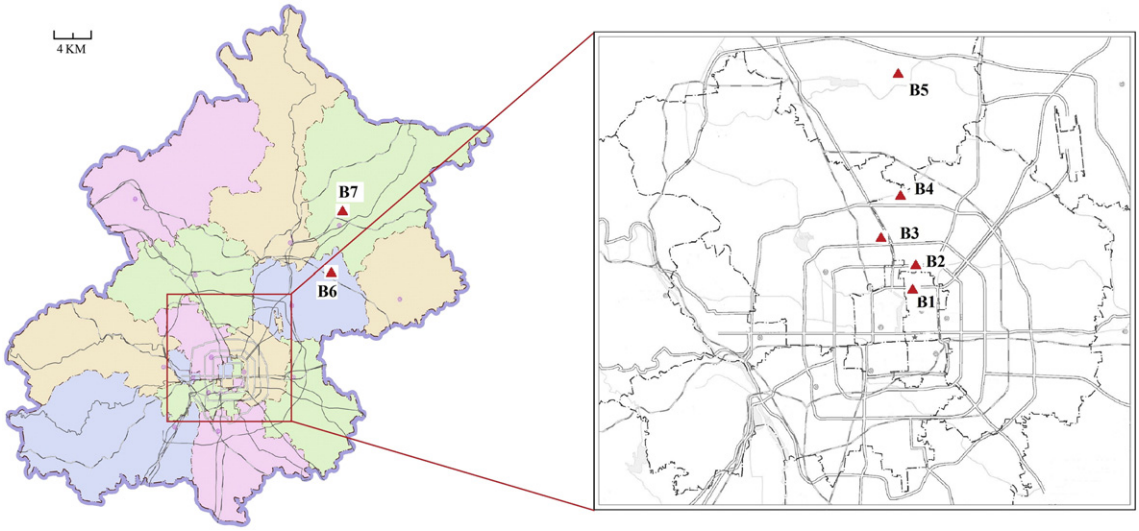

Fig. 1. Location of sampling sites in each functional areas of Beijing.

Table 1
Location and description of sampling sites in Beijing.

Sites	Latitude	Longitude	Description
B1	N:39° 56′ 48.00″	E:116° 24′ 02.86″	City central, near Hutong Scenic spot
B2	N:39° 58′ 11.34″	E:116° 24′ 06.64″	Within 3rd ring road, residential areas
B3	N:39° 59′ 14.76″	E:116° 21′ 13.18″	Within 4th ring road, schools
B4	N:40° 00′ 50.56″	E:116° 24′ 34.29″	Within 5th ring road, Olympic Park
B5	N:40° 09′ 22.86″	E:116° 26′ 22.00″	Rural countryside, near factory
B6	N:40° 11′ 22.94″	E:116° 52′ 40.11″	Shunyi District, inner suburban district
B7	N:40° 21′ 46.51″	E:116° 49′ 27.50″	Miyun County, ecological reserve, background

RH) before sampling. The scale used for weighing purposes is accurate to one hundred thousandth of a gram (XP105DR, Mettler-Toledo, Switzerland). A total of 13 samples were obtained from the whole process. Two samples were collected at each site (except for B5). Due to weather conditions, we only collected one sample at B5 under haze fog weather. All the filters were airproofed in tin foil packages following sampling. After weighing, the filters were stored at −20 °C until analysis (Gao et al., 2015).

2.3. Trace element analysis

To guarantee the accuracy of the experiment, samples were sent to Beijing Research Institute of Uranium Geology. Detailed steps of trace element analysis can be found in a previous study (Gao et al., 2015). Clean scissors were employed to cut half of each membrane and ICP-MS was adopted to identify concentrations of trace metals (Cu, Ce, Cd, Zn, Pb, Ni, Cr, Ba, V and Sb). After the shredded filters were transferred into a 25 mL PTFE (polytetrafluoroethylene) vial, 7 mL of HNO_3 and 3 mL of $HClO_4$ were added to the vial. At last, the vessel was covered with a steel jar outside and placed in a microwave digestive system (MK-III, Sinco Institute of Microwave Dissolving and Testing Techniques, China). Pressure and temperature profiles in the vessels were monitored on an external computer to better assess their effects on sample digestion. Effective digestions were achieved by setting the microwave program and power settings so that temperature was always the controlling parameter (Kingston and Haswell, 1997). The tank was baked in the microwave digestive system for about 24 h with the temperature being maintained at 100 °C, so as to fully dissolve the sample. And then, the temperature was increased to 260 °C until white smoke appeared. After being digested and cooled, 3 mL of remaining solution was transferred to a 15 mL volumetric flask. In the next step, the flask was calibrated at the final volume by employing a buffer solution. Subsequently, the solution was measured through the application of ICP-MS (VG PQ ExCell, Thermo Fisher Scientific Inc., USA). For quality control of elemental analysis, detection limits were estimated using five blank filter solutions. In addition, the method described above was employed to digest and analyze blank filters with 0.1 g mL^{-1} NIST Standard Reference Material 1648a. Samples were analyzed more than twice to check for reproducibility and reduce measurement errors. The detection limits of these metals varied from 0.01 ng m^{-3} (Cd) to 1.31 ng m^{-3} (Zn). The experiment results indicated that the recovery rates were between 85% and 110%, which were within the error range. The whole experiment process was in strict accordance with the Methods for Chemical Analysis of Silicate Rocks-Part 30: Determination of 44 Elements (Wang et al., 2013; PRC National Standard, 2010; Gao et al., 2015).

2.4. PAH analysis

Details of the methods used for PM2.5 sample extraction can be found in many previous studies (Tham et al., 2008; Dallarosa et al., 2008; Amador-Muñoz et al., 2013). The samples of filter aliquots were ultrasonically extracted three times for 15 min each with dichloromethane/methanol (2:1, v:v). After filtering, the solvent extracts were combined and concentrated on a rotary evaporator; the extract was reduced to 1 mL with dry nitrogen gas. Aliquots of these extracts were reacted with BSTFA, containing 1% trimethyl-chlorosilane and pyridine for 3 h at 70 °C to derivatize COOH and OH groups to their corresponding trimethylsilyl esters and ethers, respectively. The silylated extracts were dried with N2 to remove the remaining BSTFA and pyridine, and then added to n-hexane and internal standards before injection in the gas chromatograph. An Agilent/HP 6890 gas chromatograph (GC; Agilent/Hewlett-Packard, Santa Clara, CA, USA) equipped with a 50-m HP-5 capillary column coupled to a Micromass VG Platform II mass spectrometer (MS; Waters, Manchester, UK) operated on the electron impact mode (70 eV) was used to analyze the concentrations of PAHs. Five blank samples were measured under the same conditions to determine any background contamination. All samples were analyzed more than twice to reduce measurement errors. The average recoveries of 14 PAHs varied from 71% to 101%. Because of low recovery, the result of naphthalene (38% for recovery) was not concluded in this study. The PAH analysis included acenaphthene (ACE), fluorine (FLO), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benz(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenz(a,h) anthracene (DahA), indeno(1,2,3-cd)pyrene (IcdP) and benzo(g,h,i) perylene (BghiP).

2.5. Methods of health risk assessment

Residential exposure of heavy metal and PAHs can occur via three main ways: inhalation, direct ingestion and dermal adsorption (Zheng et al., 2010). In this study, health risk assessment was calculated on the base of inhalation of suspended particles through the mouth and nose. According to the International Agency for Research on Cancer (IARC), pollutants were divided into non-carcinogens and carcinogens. Among the evaluated compositions, FLO, FLA, PYR, ANT, Cu, Pb, Zn and V were considered as non-carcinogenic, while DahA, BkF, BbF, IcdP, CHR,

Table 2
Reaction parameters for heavy metals and PAHs entering the human body through the respiratory system.

Element	Nature	SF [mg·(kg day)$^{-1}$]$^{-1}$	RfC mg·(kg day)$^{-1}$	RfD mg·(kg day)$^{-1}$
Cd	Carcinogenic	8.40		
Cr	Carcinogenic	42.0		
Ni	Carcinogenic	0.84		
Pb	Non-carcinogenic			$3.5 * 10^{-3}$
Cu	Non-carcinogenic			$1.43 * 10^{-2}$
Zn	Non-carcinogenic			0.3
V	Non-carcinogenic			$7 * 10^{-3}$
DahA	Carcinogenic	4.20		
BkF	Carcinogenic	0.385		
BbF	Carcinogenic	0.358		
IcdP	Carcinogenic	0.385		
CHR	Carcinogenic	0.0385		
BaA	Carcinogenic	0.385		
BaP	Carcinogenic	3.85		
FLO	Non-carcinogenic		0.04	
ANT	Non-carcinogenic		0.3	
FLA	Non-carcinogenic		0.04	
PYR	Non-carcinogenic		0.03	

Table 3
PAH concentrations at different sampling sites under HF/NHF conditions.

Sites/ng m^{-3}	ACY	FLO	PHE	ANT	FLA	PYR	BaA	CHR	BbF	BkF	BaP	IcdP	DahA	BghiP	Sum
B1	11.89	0	16.84	14.96	21.32	23.26	32.71	30.49	23.67	27.77	34.99	0	0	0	237.89
BH1	0	0	14.55	17.09	21.65	22.53	32.41	31.69	26.57	27.03	35.44	32.71	35.46	9.66	306.78
B2	0	0	7.73	7.56	16.49	0	0	0	0	0	0	0	0	0	31.78
BH2	0	0	8.05	7.54	12.60	12.65	16.92	17.44	12.01	13.55	18.04	0	0	0	118.79
B3	11.78	0	0	0	25.05	0	0	0	0	0	0	0	0	0	36.83
BH3	0	14.23	21.65	0	31.76	31.29	43.38	50.57	33.13	29.67	40.21	40.91	35.93	15.25	387.99
B4	11.75	0	0	0	22.21	24.05	32.80	32.49	25.39	30.05	36.02	32.87	0	9.72	257.36
BH4	0	0	0	0	34.61	34.12	49.03	49.17	37.83	42.95	52.86	0	0	0	300.58
BH5	0	0	0	0	44.29	50.07	73.69	80.97	58.70	58.42	73.63	0	0	0	439.77
B6	0	0	0	0	49.08	0	64.94	58.36	47.00	54.41	0	0	0	0	273.79
BH6	0	0	0	0	41.89	44.82	65.39	63.75	48.83	53.59	70.55	0	0	0	388.82
B7	0	0	15.72	15.80	20.78	23.56	34.88	37.95	27.67	30.32	36.40	33.64	0	9.93	286.64
BH7	0	0	0	0	28.38	0	34.08	32.28	24.48	30.87	35.61	0	0	0	185.71
Average	2.72	1.09	6.50	4.84	28.47	20.49	36.94	37.32	28.10	30.66	33.37	10.78	5.49	3.43	250.21
SD	5.18	3.95	8.09	6.92	11.21	17.19	22.97	23.58	17.62	18.72	24.21	16.94	13.41	5.52	128.01

BaA, BaP, Cr, Ni and Cd were carcinogenic. In this paper, we used the health risk assessment model recommended by USEPA (EPA, 1989). For carcinogens, normal average daily dose (ADD, mg kg^{-1} day^{-1}) for inhalation exposure route was used in the assessment of cancer risk, while the life time average daily dose (LADD, mg kg^{-1} day^{-1}) was used for non-carcinogens.

$$\text{ADD (or LADD)} = (C \times IR \times EF \times ED)/(BW \times AT) \quad (1)$$

$$HQ = ADD/RfD \quad (2)$$

$$HQ = ADD/RfC \quad (3)$$

$$ILCR = LADD \times SF \quad (4)$$

To guarantee the result of the health risk assessment more accurate, suitable exposure parameters were chosen from Exposure Factor Handbooks and existing researches in this study for the Chinese population. C: represents concentration of pollutants (mg m^{-3}); IR: respiration rate (m^3 day^{-1}), in this study, 19.2 m^3 day^{-1} for men, 14.17 m^3 day^{-1} for women and 5.00 m^3 day^{-1} for children; EF: exposure frequency (day a^{-1}), 350 days a^{-1} for both adults and children; ED: duration of exposure (day), 30 days for adults and 6 days for children; BW: bodyweight (kg), in this study, 62.7, 54.4 and 15 kg for men, women and children respectively; AT: the average exposure time (day), for carcinogens, 70 * 365 days was used for both adults and children; when considering non-carcinogens, 30 * 365 and 6 * 365 days were used for adults and children respectively. RfD: the reference dose for metal (mg kg^{-1} day^{-1}); RfC: the reference dose for PAHs (mg kg^{-1} day^{-1}), showed in Table 2. SF: the reciprocal value of the level of intensity of carcinogenic chemicals ((mg kg^{-1} day^{-1})$^{-1}$), showed in Table 3 (EPA, 1989, 2011; Wang et al., 2009; Li et al., 2013; Gao et al., 2015). Hazard quotient (HQ) which was considered as hazard quotient for non-carcinogenic risks (dimensionless value), can be calculated from the equation above. If the value of HQ is greater than 1, the risk of cancer exists. When the HQ is less than or equal to 1, the risk of cancer can be considered less, or can be ignored. The incremental lifetime cancer risk (ILCR) was calculated to evaluate the cancer risk caused by carcinogens. ILCR is the average annual excess risk of cancer for an individual, dimensionless. When ILCR is greater than 10^{-4}, it suggested that the potential risk of cancer exists seriously. If the ILCR was less than 10^{-6}, the risk caused by carcinogens can be ignored (Gao et al., 2015; Chen et al., 2015; Zheng et al., 2010).

2.6. Quality control (QC) and quality assurance (QA)

All data in the study were subjected to strict quality-control procedures to minimize sampling/measurement errors. A number of field and laboratory blanks were taken during the pre-treatment, ICP-MS and GC–MS analysis steps. And these blank samples were measured everyday under the same conditions as real samples. Samples were analyzed more than twice to check for reproducibility and reduce measurement errors. In this study, concentrations of metals and PAHs below the detection limit were excluded from discussion. The average recoveries of the indicators were from 70.32 to 121.65% for the experimental process.

3. Results and analysis

3.1. Ambient concentrations of PM2.5

Fig. 2 presents the mass concentrations of PM2.5 obtained from samples in Beijing. In the samples collected from B1 to B7 site, PM2.5 concentrations fluctuated between 29.17 μg m^{-3} and 276.39 μg m^{-3} with an average value of 117.85 μg m^{-3}. Besides, under haze–fog (hereafter called HF) conditions, the PM2.5 concentration ranged from 47.91 μg m^{-3} to 276.39 μg m^{-3}, while the corresponding value under non-haze–fog (hereafter called NHF) weather was between 29.17 μg m^{-3} and 78.47 μg m^{-3}. Similar research conducted in Beijing manifests that the daily average PM2.5 concentration was 159 μg m^{-3} in 2013 (Huang et al., 2014). When compared with this level, the concentrations observed in this study were generally lower. But all the PM2.5 levels under HF conditions significantly exceeded the outdoor average PM2.5 daily limit (75 μg m^{-3}, level II) according to the National Ambient Air Quality Standard of China (hereafter called NAAQS) (PRC National Standard, 2012). As a contrast, when it came across NHF weathers, all the data except the city central (B1 site, a little bit higher than limit) were within the limit. It suggested that when the weather

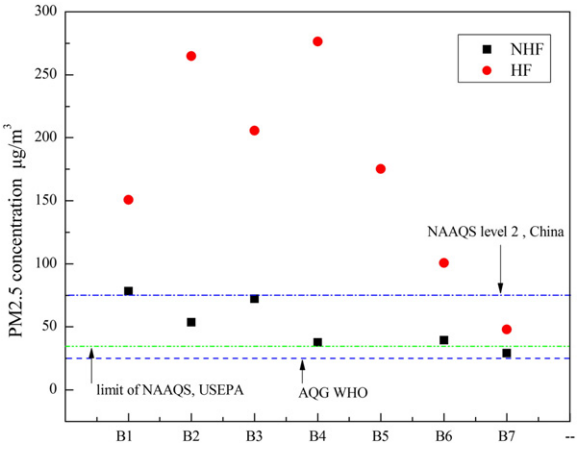

Fig. 2. Daily concentration of PM2.5 in B1–B7 sampling sites.

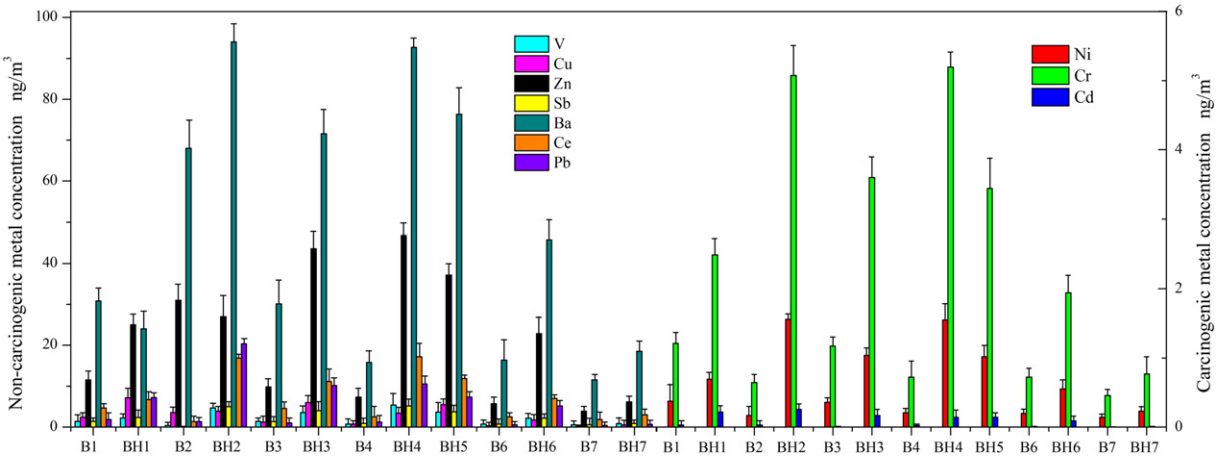

Fig. 3. Variety of non-carcinogenic and carcinogenic heavy metal concentration at each functional area in Beijing. (BH represented sampling event under haze fog conditions.)

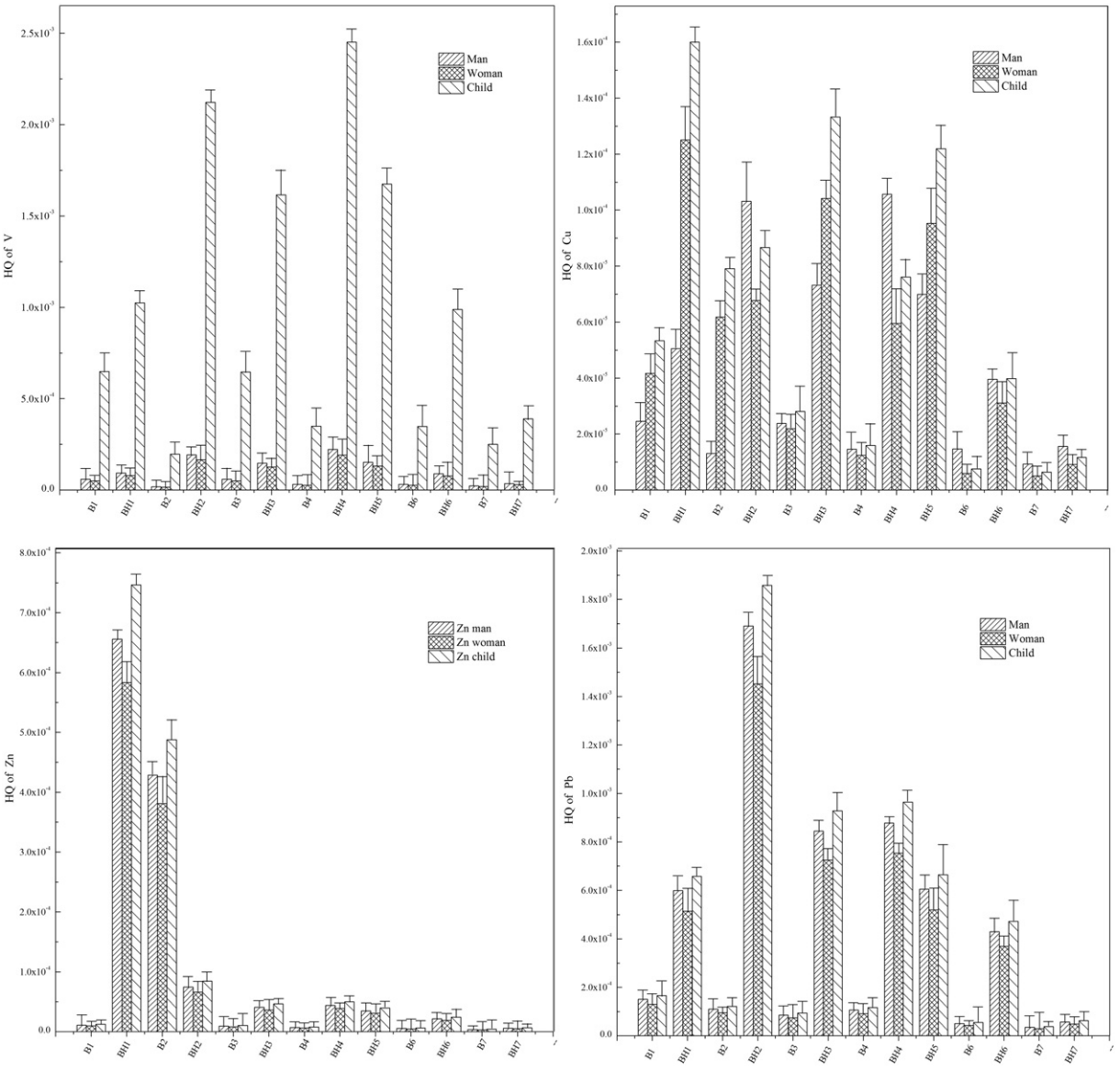

Fig. 4. The risk associated with non-carcinogenic heavy metal components of PM2.5 for different demographic groups. (BH represented sampling event under haze fog conditions.)

condition was good, the various functional areas of Beijing's air quality were qualified. Furthermore, the maximum concentration that occurred at the B4 site (near under HF weather) was 3.68 times the relevant limit, and it was worth noting that the corresponding sampling site was located near Olympic park which was considered as an urban green space and scenic area in Beijing. The PM2.5 concentrations observed in each functional area significantly exceeded the air quality guideline of the World Health Organization (here after called AQG WHO, 25 μg m^{-3}), and all the values were beyond the limit level of the National Ambient Air Quality Standards of the United States (here after called NAAQS USA, 35 μg m^{-3}) except the B7 site (USEPA, 2006). It was consistent with previous research results that Miyun county, which was far away from city central and considered as ecological reserve areas, suffered less particulate matter pollution (Gao et al., 2015). The high PM2.5 concentrations in urban areas were associated with high relative humidity and the low temperature that probably inhibited the dispersion of pollutants in winter Beijing. It was important to note that residential areas and schools also suffered from serious particle pollution under HF days. What's more, the particle pollution matter in Beijing was comparable to Ahmedabad, India where PM2.5 mass concentration ranged from 32 to 106 μg m^{-3} (Rengarajan et al., 2011). But, when compared with Yokohama, Japan (3.63–47.78 μg m^{-3}), particle pollution level was high in urban Beijing (Khan et al., 2010). The PM2.5 pollution was significant lower than other seasons (Sun et al., 2013). Based on the analysis above, particulate matter pollution was still serious in winter Beijing, especially under HF conditions.

3.2. Elemental compositions

Half of a sampling membrane was analyzed to investigate metal element compositions. All the 10 estimated trace metals were significant higher than their instrumental detection limit. Fig. 3 showed that the mass concentrations of non-carcinogenic and carcinogenic metals in PM2.5 fluctuated significantly at each functional area under HF and NHF conditions. BH1–7 means samples collected under HF conditions. According to analytical result, it was evident that Zn and Ba showed the highest concentration levels in the non-carcinogenic metals, followed by Ce > Pb > Cu > V > Sb with the same trend being found at all functional areas in Beijing. The mass concentration of most elements at each area varied with consistency, and this result indicated that most sampling sites may be affected by the same source. The total concentration of the ten measured elements at each functional area ranged from 0.02 to 1.14 μg m^{-3}. The data manifest that during HF days, city central (B1, 1.05 μg m^{-3}) presented the highest total concentration of

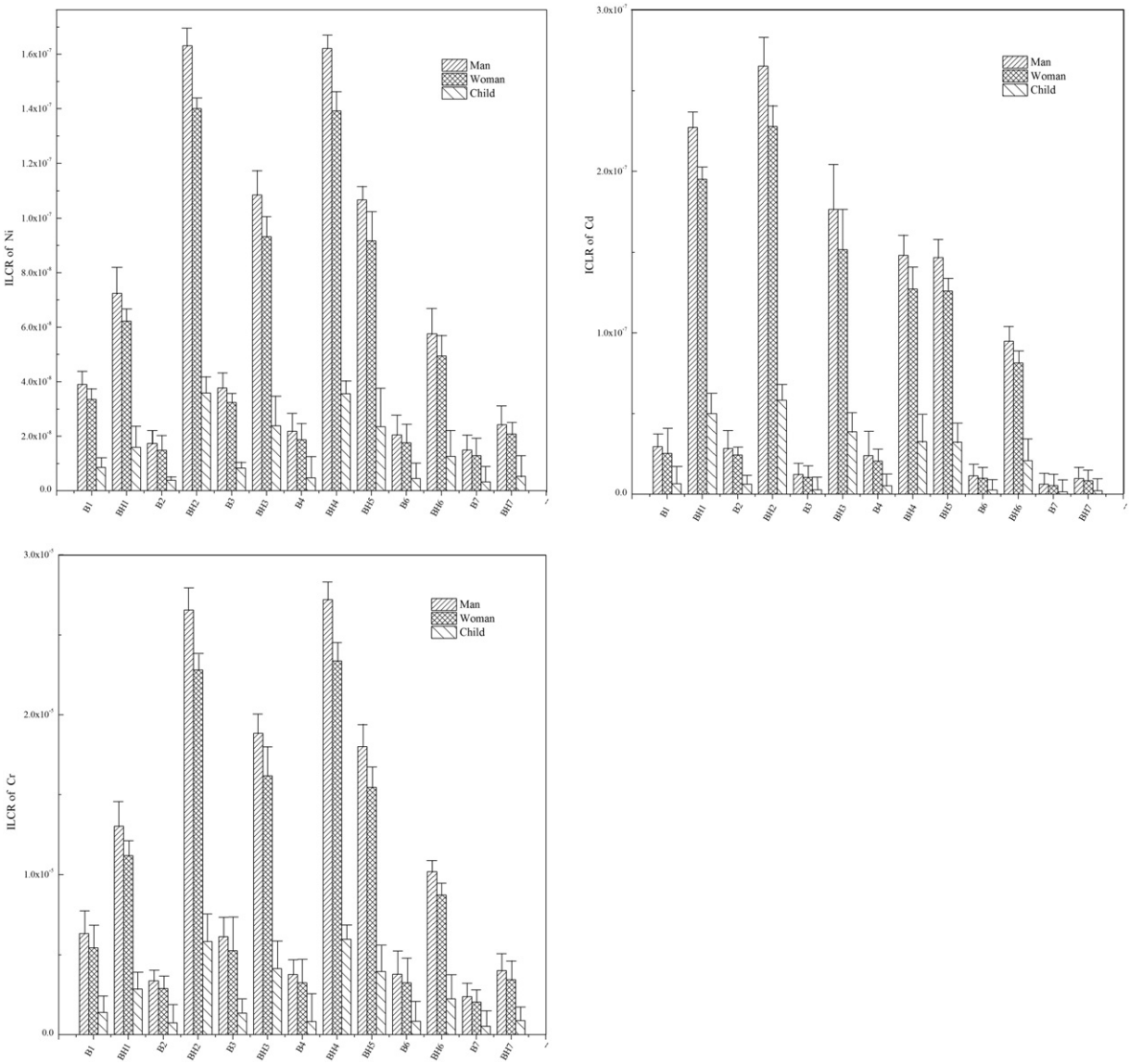

Fig. 5. The risk associated with carcinogenic heavy metal components of PM2.5 for different demographic groups. (BH represented sampling event under haze fog conditions.)

metals, followed by residential areas (B2, 0.25 μg m^{-3}) > Olympic Park (B4, 0.20 μg m^{-3}) > schools (B3, 0.16 μg m^{-3}) > rural countryside (B5, 0.15 μg m^{-3}) > inner suburban district (B6, 0.09 μg m^{-3}) > ecological reserve (B7, 0.03 μg m^{-3}). While the corresponding sequence under NHF days was residential areas (B2, 1.13 μg m^{-3}) > city central (B1, 0.05 μg m^{-3}) > schools (B3, 0.04 μg m^{-3}) > Olympic Park (B4, 0.021 μg m^{-3}) > inner suburban district (B6, 0.020 μg m^{-3}) > ecological ecological reserve (B7, 0.019 μg m^{-3}). During NHF days, higher metal concentrations in residential areas were mainly affected by human activities around. It can be concluded that under the same conditions, metal concentration was higher in central area than the value in suburb.

During HF period, residential areas (B2) presented the highest total concentration of carcinogenic metals, followed by Olympic Park (B4) > schools (B3) > city central (B1) > rural countryside (B5) > inner suburban district (B6) > ecological reserve (B7), while the order under NHF weathers was followed by city central > residential areas > Olympic Park > inner suburban district > schools > ecological reserve. It was important to note that compared with other functional areas, residential areas, schools and Olympic Park suffered higher carcinogenic metal concentrations in winter. As the B6 and B7 sites were far away from city central, carcinogenic metal levels were relative low in these functional areas. Besides, the average total concentration of carcinogenic metals at seven areas was 4.31 ng m^{-3} under HF conditions and was 1.07 ng m^{-3} in NHF days, which respectively accounted for 2.67% and 2.58% of the ten observed metal concentrations. This result indicated that the proportion of carcinogenic metals was relatively stable in each functional area in winter. Compared with other cities, daily mean concentrations of Cr, Ni and Cd in Beijing were equal to those in Milan and average values of these metals were significant lower than those serious polluted metropolises in China and other Asian countries (Vecchi et al., 2004; Deng et al., 2006).

3.3. PAH concentration

Fourteen PAHs were detected in the PM2.5 samples. They were ACE, FLO, PHE, ANT, FLA, PYR, BaA, CHR, BbF, BkF, BaP, DahA, IcdP and BghiP. The concentrations of the fourteen PAHs are presented in Table 3. The average concentrations of individual 14 PAHs varied from 1.09 to 37.32 ng m^{-3}, while the concentration of their sum (Σ_{14}PAHs) ranged from 31.78 to 439.77 ng m^{-3}, with a mean of 250.21 ± 128.01 ng m^{-3}. These results were about 4–8 times higher than those for summer in Guangzhou, a city in the south of China, but only 2–3 times those for winter (Wei et al., 2012). They were also much higher than those measured in Harbin, a city in the northeast China (Ma et al., 2010). The mean concentrations of PAHs in this study were 50% higher than those recorded from January to March 2006, and 2–3 times the values for September 2008 and July 2009 (Tao et al., 2007; Ma et al., 2011). In Fig. 2, higher ring PAHs (with four to six rings) were the dominant species, with FLA, PYR, BaA, CHR, BbF, BkF, and BaP constituting more than 90% of the Σ_{14}PAHs. This result was consistent with other studies (Ma et al., 2011; Chen et al., 2011).

Comparing the concentrations of Σ_{14}PAHs for each functional area under HF and NHF conditions, results showed that the concentrations under HF weather were higher, except for the B7 site which was located in Miyun and considered as background. Miyun (B7) is a relatively rich area of organic matter in the environment (Lu et al., 2013). It was different with the metal concentration order that rural countryside (BH5) presented the maximum concentration of Σ_{14}PAHs, followed by inner suburban district (BH6) > schools (BH3) > city central (BH1) > Olympic Park (BH4) > ecological reserve (BH7) > residential areas (BH2). Data suggested that under HF conditions, organic pollution at inner suburban district was serious than other functional areas, and this result may be caused by factories near suburbs. Interestingly, the minimum concentration in non-haze samples was 31.78 ng m^{-3} and 36.83 ng m^{-3} at residential areas and schools, while the maximum value under HF conditions was 439.3 ng/m^3 in Shunyi district. The

Table 4
The risk associated with non-carcinogenic PAH components of PM2.5 for different demographic groups. (BH represented sampling event under haze fog conditions. The bold figures represented values under HF conditions.)

	Men					Women					Children				
	FLO	ANT	FLA	PYR	FLO	ANT	FLA	PYR	FLO	ANT	FLA	PYR	Average
B1	0	1.45×10^{-5}	1.55×10^{-4}	2.26×10^{-4}	0	1.24×10^{-5}	1.33×10^{-4}	1.94×10^{-4}	0	1.59×10^{-5}	1.7×10^{-4}	2.47×10^{-4}	9.74×10^{-5}
BH1	**0**	$\mathbf{1.66 \times 10^{-5}}$	$\mathbf{1.57 \times 10^{-4}}$	$\mathbf{2.18 \times 10^{-4}}$	**0**	$\mathbf{1.42 \times 10^{-5}}$	$\mathbf{1.35 \times 10^{-4}}$	$\mathbf{1.88 \times 10^{-4}}$	**0**	$\mathbf{1.82 \times 10^{-5}}$	$\mathbf{1.73 \times 10^{-4}}$	$\mathbf{2.40 \times 10^{-4}}$	$\mathbf{9.67 \times 10^{-5}}$
B2	0	7.33×10^{-6}	1.2×10^{-4}	0	0	6.29×10^{-6}	1.02×10^{-4}	0	0	8.05×10^{-6}	1.32×10^{-4}	0	3.14×10^{-5}
BH2	**0**	$\mathbf{7.31 \times 10^{-6}}$	$\mathbf{9.16 \times 10^{-5}}$	$\mathbf{1.23 \times 10^{-4}}$	**0**	$\mathbf{6.27 \times 10^{-6}}$	$\mathbf{7.86 \times 10^{-5}}$	$\mathbf{1.05 \times 10^{-4}}$	**0**	$\mathbf{8.03 \times 10^{-6}}$	$\mathbf{1.01 \times 10^{-4}}$	$\mathbf{1.34 \times 10^{-4}}$	$\mathbf{5.46 \times 10^{-5}}$
B3	0	0	1.82×10^{-4}	0×	0	0	1.56×10^{-4}	0	0	0	2.00×10^{-4}	0	4.49×10^{-5}
BH3	$\mathbf{1.04 \times 10^{-4}}$	**0**	$\mathbf{2.31 \times 10^{-4}}$	$\mathbf{3.03 \times 10^{-4}}$	$\mathbf{8.89 \times 10^{-5}}$	**0**	$\mathbf{1.98 \times 10^{-4}}$	$\mathbf{2.61 \times 10^{-4}}$	$\mathbf{1.14 \times 10^{-4}}$	**0**	$\mathbf{2.54 \times 10^{-4}}$	$\mathbf{3.33 \times 10^{-4}}$	$\mathbf{1.57 \times 10^{-4}}$
B4	0	0	1.62×10^{-4}	2.33×10^{-4}	0	0	1.38×10^{-4}	2.00×10^{-4}	0	0	1.78×10^{-4}	2.56×10^{-4}	9.73×10^{-5}
BH4	**0**	**0**	$\mathbf{2.52 \times 10^{-4}}$	$\mathbf{3.31 \times 10^{-4}}$	**0**	**0**	$\mathbf{2.16 \times 10^{-4}}$	$\mathbf{2.84 \times 10^{-4}}$	**0**	**0**	$\mathbf{2.77 \times 10^{-4}}$	$\mathbf{3.63 \times 10^{-4}}$	$\mathbf{1.44 \times 10^{-4}}$
BH5	**0**	**0**	$\mathbf{3.22 \times 10^{-4}}$	$\mathbf{4.86 \times 10^{-4}}$	**0**	**0**	$\mathbf{2.76 \times 10^{-4}}$	$\mathbf{4.17 \times 10^{-4}}$	**0**	**0**	$\mathbf{3.54 \times 10^{-4}}$	$\mathbf{5.33 \times 10^{-4}}$	$\mathbf{1.99 \times 10^{-4}}$
B6	0	0	3.57×10^{-4}	0	0	0	3.06×10^{-4}	0	0	0	3.92×10^{-4}	0	8.80×10^{-5}
BH6	**0**	**0**	$\mathbf{3.05 \times 10^{-4}}$	$\mathbf{4.35 \times 10^{-4}}$	**0**	**0**	$\mathbf{2.61 \times 10^{-4}}$	$\mathbf{3.73 \times 10^{-4}}$	**0**	**0**	$\mathbf{3.35 \times 10^{-4}}$	$\mathbf{4.77 \times 10^{-4}}$	$\mathbf{1.82 \times 10^{-4}}$
B7	0	1.5×10^{-5}	1.51×10^{-4}	2.28×10^{-4}	0	1.31×10^{-5}	1.29×10^{-4}	1.96×10^{-4}	0	1.68×10^{-5}	1.66×10^{-4}	2.51×10^{-4}	9.73×10^{-5}
BH7	**0**	**0**	$\mathbf{2.06 \times 10^{-4}}$	**0**	**0**	**0**	$\mathbf{1.77215 \times 10^{-4}}$	**0**	**0**	**0**	$\mathbf{2.27 \times 10^{-4}}$	**0**	$\mathbf{5.09 \times 10^{-5}}$
Average	7.96×10^{-6}	4.69×10^{-6}	2.07×10^{-4}	1.99×10^{-4}	6.84×10^{-6}	4.03×10^{-6}	1.77×10^{-4}	1.71×10^{-4}	8.75×10^{-6}	5.16×10^{-6}	2.28×10^{-4}	2.18×10^{-4}	1.03×10^{-4}
SD	2.87×10^{-5}	6.7×110^{-6}	8.15×10^{-5}	1.67×10^{-4}	2.47×10^{-5}	5.76×10^{-6}	6.99×10^{-5}	1.43×10^{-4}	3.15×10^{-5}	7.37×10^{-6}	8.96×10^{-5}	1.83×10^{-4}	5.32×10^{-5}

range in concentrations under NHF conditions (31.78–273.79 ng m^{-3}) was slightly higher than for Beijing in 2009 (Wu et al., 2014). The concentrations of HF samples presented significant high levels, ranging from 118.79 to 439.77 ng m^{-3}, about 2–3 times the values for NHF conditions. This result suggested that under non-haze conditions, the air quality in Beijing was comparable to other Chinese cities, but during hazy days, the air pollution was serious (Zhang et al., 2007; Zhang et al., 2008). In this study, PAH concentrations were significantly higher than the level reported abroad (Guzmán-Torres et al., 2009; Tham et al., 2008).

3.4. Heavy metal risk assessment

Fig. 4 indicated that in Beijing, the average risk level of non-carcinogenic heavy metals for exposure through the respiratory system fluctuated from 3.25×10^{-5} (Zn for women) to 2.45×10^{-3} (V for children). Whether it was for men and women, Pb (4.34×10^{-4} and 3.73×10^{-4} respectively) presented the maximum average HQ at each functional areas, followed by Zn > V > Cu. But the order for children was V > Pb > Zn > Cu. For both adults and children, high risk levels all occurred on HF days in urban and rural Beijing. However, when it underwent NHF days, the HQ of all the functional areas exhibited lower values. For instance, average values of HQ for men under HF period were about 3.61 (for V), 3.92 (for Cu), 1.62 (for Zn), and 8.12 (for Pb) times higher than the value of NHF days. Besides, this multiple relationship was similar for women and children. During HF period, the risk levels of Pb for men occurred in the decreasing order of residential areas (B2), Olympic Park (B4), schools (B3), city central (B1), rural countryside (B5), inner suburban district (B6) and ecological reserve (B7). The cause of this result may be more traffic in urban areas than suburbs, especially for residential areas where large population and traffic jams existed. Similarly, regardless of whether it was for adults or children, the suburb including rural countryside (B5), inner suburban district (B6) and ecological reserve (B7) had lower HQ values than other functional areas. This result could reflect less atmospheric environment pollution in rural suburb than in urban. What's more, Cu posed the greatest cancer risk to children, followed by women and then men, but other non-carcinogenic substances occurred in the decreasing order of children, men and women. Although Pb presented the maximum HQ, it was still within the limit level and didn't cause harm to human health. When compared with polluted areas in China, the risk level caused by Pb and Zn was low (Zheng et al., 2010).

As shown in Fig. 5, the average risk level of carcinogenic heavy metals for exposure through the respiratory system respectively ranged from 1.37×10^{-9} (Cd for children) to 2.72×10^{-5} (Cr for men). Whether it was for men, women or children, Cd (1.10×10^{-5}, 9.48×10^{-6} and 2.43×10^{-6} respectively) presented the maximum average ILCR at all the sampling sites, followed by Cd > Ni. The average ILCR of Cd and Ni was obviously lower than 10^{-6}, while the corresponding value of Cr (for men and women) was between 10^{-6} and 10^{-4}, which suggested that the risk levels of Cd and Ni were under average risk acceptance and to some extent, Cr may have a potential risk to the environment. Compared with NHF days, carcinogenic heavy metals could more easily cause harm to residence under HF conditions in Beijing. For instance, average values of ILCR for men under HF period were about 3.92 (for Ni and Cr), 8.21 (for Cd) times higher than the value of NHF days at each functional area. Under HF conditions, Olympic Park (B4) presented the maximum risk level among all the city functional areas, then followed by residential areas (B2) > schools (B3) > rural countryside (B5) > city central (B1) > inner suburban district (B6) > ecological reserve (B7). Besides, during HF period, the risk levels of Cr at residential areas (B2), schools (B3), Olympic Park (B4) and rural countryside (B5) exceeded the limit of 10^{-6} for both men and women. There were large numbers of residential areas, scenic areas and outdoor sports venues near these city functional areas. Different risk tendencies to men, women and children between carcinogenic and non-carcinogenic can be demonstrated by individual differences in respiration rate, outdoor exposure and body weight (Gao et al., 2015). When compared with non-carcinogenic heavy metals, the risk levels of carcinogenic heavy metals to adults and children were different. All the carcinogenic metals could cause harm to men more easily, followed by women and then children. In this study, carcinogenic risks attributed to Cr, Cd and Ni pollution were much lower than the value found in contaminative areas in China (Cao et al., 2014, 2015). In Beijing, the risk posed by carcinogenic and non-carcinogenic metals was significantly lower than that in numerous cities in China and other Asia cities (Zheng et al., 2010; Sharma and Maloo, 2005).

3.5. PAH risk assessment

Data collected in Beijing manifested that the average risk level of non-carcinogenic PAHs for exposure through the respiratory system fluctuated between 3.14×10^{-5} and 1.99×10^{-3} at seven sampling sites (Table 4). Generally speaking, non-carcinogenic PAHs posed the greatest cancer risk to children, followed by men and then women. Unlike the health risk assessment of heavy metals, FLA presented the maximum value for both adults and children, then followed by PYR > FLO > ANT. In addition to the above difference, risk level of non-carcinogenic PAHs under NHF conditions also exhibited in the same order of magnitude with HF values. Under HF conditions, rural countryside (B5) showed the highest risk value, followed by inner suburban district (B6), schools (B3), Olympic Park (B4), city central (B1),

Table 5
The risk associated with carcinogenic PAH components of PM2.5 for different men. (The bold figures represented that values exceed the limit 10^{-6}.)

	Men						
	BaA	CHR	BbF	BkF	BaP	IcdP	DahA
B1	1.57E−06	1.46E−07	1.14E−06	1.33E−06	**1.67E−05**	0	0
BH1	1.56E−06	1.52E−07	1.28E−06	1.29E−06	**1.70E−05**	1.57E−06	**1.86E−05**
B2	0	0	0	0	0	0	0
BH2	8.12E−07	8.37E−08	5.76E−07	6.501E−07	8.65E−06	0	0
B3	0	0	0	0	0	0	0
BH3	2.08E−06	2.43E−07	1.59E−06	1.42E−06	**1.92E−05**	1.96E−06	**1.88E−05**
B4	1.57E−06	1.56E−07	1.22E−06	1.44E−06	**1.72E−05**	1.58E−06	0
BH4	2.35E−06	2.36E−07	1.82E−06	2.06E−06	**2.53E−05**	0	0
BH5	3.54E−06	3.89E−07	2.82E−06	2.80E−06	**3.53E−05**	0	0
B6	3.12E−06	2.8E−07	2.26E−06	2.61E−06	0	0	0
BH6	3.14E−06	3.06E−07	2.34E−06	2.57E−06	**3.38E−05**	0	0
B7	1.67E−06	1.82E−07	1.33E−06	1.45E−06	**1.74E−05**	1.61E−06	0
BH7	1.64E−06	1.55E−07	1.17E−06	1.48E−06	**1.70E−05**	0	0
Max	3.54E−06	3.89E−07	2.82E−06	2.80E−06	3.53E−05	1.96E−06	1.88E−05
Average	1.77E−06	1.79E−07	1.35E−06	1.47E−06	**1.60E−05**	5.17E−07	2.88E−06
SD	1.1E−06	1.13E−07	8.45E−07	8.98E−07	1.16E−05	8.13E−07	7.02E−06

Table 6
The risk associated with carcinogenic PAHs components of PM2.5 for different women. (The bold figures represented that values exceed the limit 10^{-6}.)

	Women						
	BaA	CHR	BbF	BkF	BaP	IcdP	DahA
B1	1.35E−06	1.26E−07	9.76E−07	1.14E−06	**1.44E−05**	0	0
BH1	1.34E−06	1.31E−07	1.1E−06	1.11E−06	**1.46E−05**	1.35E−06	**1.59E−05**
B2	0	0	0	0	0	0	0
BH2	6.97E−07	7.19E−08	4.95E−07	5.58E−07	7.43E−06	0	0
B3	0	0	0	0	0	0	0
BH3	1.79E−06	2.08E−07	1.37E−06	1.22E−06	**1.65E−05**	1.69E−06	**1.62E−05**
B4	1.35E−06	1.34E−07	1.05E−06	1.23E−06	**1.48E−05**	1.35E−06	0
BH4	2.02E−06	2.03E−07	1.56E−06	1.77E−06	**2.17E−05**	0	0
BH5	3.04E−06	3.34E−07	2.42E−06	2.40E−06	**3.03E−05**	0	0
B6	2.68E−06	2.41E−07	1.94E−06	2.24E−06	0	0	0
BH6	2.69E−06	2.63E−07	2.01E−06	2.20E−06	**2.90E−05**	0	0
B7	1.44E−06	1.56E−07	1.14E−06	1.24E−06	**1.50E−05**	1.39E−06	0
BH7	1.40E−06	1.33E−07	1.01E−06	1.27E−06	**1.46E−05**	0	0
MAX	3.04E−06	3.34E−07	2.42E−06	2.40E−06	3.03E−05	1.69E−06	1.62E−05
Average	1.52E−06	1.54E−07	1.16E−06	1.26E−06	**1.37E−05**	4.44E−07	2.47E−06
SD	9.46E−07	9.72E−08	7.26E−07	7.71E−07	9.97E−06	6.98E−07	6.03E−06

residential areas (B2) and ecological reserve (B7). High risk levels occurred at, rural countryside (B5) and inner suburban district (B6) because these functional areas were located at city faubourgs and were not far away from factories. Each functional area presented higher average risk value under HF conditions than the value in NHF days. But, it was important to note that ecological reserve (B7) didn't comply with rule. Besides, when it underwent NHF weather, Miyun areas didn't exhibit the minimum risk level, while the lowest value occurred at residential areas (B2). It may be caused by the complex organic matter environment in local Miyun. This result also reflected a less organic pollution in residential areas in urban Beijing.

As shown in Tables 5, 6 and 7, the average risk level of carcinogenic PAHs for exposure through the respiratory system respectively ranged from 6.90×10^{-7} to 2.32×10^{-6} at seven sampling sites. In HF days, the risk level of each functional area ranged in the order: rural countryside (B5) > inner suburban district (B6) > Olympic Park (B4) > city central (B1) > schools (B3) > ecological reserve (B7) > residential areas (B2). Whether it was for men, women or children, BAP (3.53×10^{-5}, 3.03×10^{-5} and 7.77×10^{-6} respectively) presented the maximum ILCR value at all the seven functional areas, followed by DahA > BkF > BbF > IcdP > CHR > BaA. Compared with NHF days, carcinogenic PAHs could easily cause harm to residence in each functional area. Take schools (B3), Olympic Park (B4) and rural countryside (B5) for instance, average values of ILCR for men under HF period were significantly higher than the value of NHF days. Residential areas (B2) where large numbers of residence existed, exhibited the minimum risk values. The average ILCR of BaP (for men and women) was between 10^{-6} and 10^{-4}, while the corresponding value of other carcinogenic PAHs was obviously lower than 10^{-6}, which suggested that the risk levels of DahA, BkF, BbF, IcdP, CHR and BaA were all under average risk acceptance and to some extent, BaP may had a potential risk to the environment. When compared with non-carcinogenic PAHs, the risk levels of carcinogenic PAHs to adults and children were different. All the carcinogenic PAHs could cause harm to men more easily, followed by women and then children. Compared with serious polluted city, risk of PAHs in Beijing was in a lower level (Xia et al., 2013; Duan et al., 2014). When compared with Malaysia where the carcinogenic risk of the total PAHs showed an acceptable risk level, the health risk was relative high in Beijing (Khan et al., 2015).

4. Conclusions

Through the analysis of data from the seven different functional areas, PM2.5 pollution in rural and urban Beijing was relative high in HF days in comparison with NHF value. Zn and Ba showed the highest concentration levels in the non-carcinogenic metals in each area. The non-carcinogenic metal concentration at all the sites ranged in the same order: Ce, Pb, Cu, V and Sb. Higher ring PAHs (with four to six rings) were the dominant species, with FLA, PYR, BaA, CHR, BbF, BkF, and BaP constituting more than 90% of the Σ_{14}PAHs. Pb (4.34×10^{-4} and 3.73×10^{-4} respectively) presented the maximum risk levels for the non-carcinogenic heavy metals at all the areas. During HF period,

Table 7
The risk associated with carcinogenic PAHs components of PM2.5 for different children.

	Children						
	BaA	CHR	BbF	BkF	BaP	IcdP	DahA
B1	3.45E−07	3.22E−08	2.5E−07	2.92E−07	3.69E−06	0	0
BH1	3.42E−07	3.34E−08	2.8E−07	2.85E−07	3.73E−06	3.45E−07	4.08E−06
B2	0	0	0	0	0	0	0
BH2	1.78E−07	1.84E−08	1.27E−07	1.42E−07	1.90E−06	0	0
B3	0	0	0	0	0	0	0
BH3	4.58E−07	5.33E−08	3.49E−07	3.12E−07	4.24E−06	4.32E−07	4.13E−06
B4	3.46E−07	3.43E−08	2.68E−07	3.16E−07	3.79E−06	3.47E−07	0
BH4	5.17E−07	5.19E−08	3.99E−07	4.53E−07	5.57E−06	0	0
BH5	7.77E−07	8.54E−08	6.19E−07	6.16E−07	7.76E−06	0	0
B6	6.85E−07	6.16E−08	4.96E−07	5.73E−07	0	0	0
BH6	6.9E−07	6.72E−08	5.15E−07	5.65E−07	7.44E−06	0	0
B7	3.68E−07	4E−08	2.92E−07	3.19E−07	3.83E−06	3.55E−07	0
BH7	3.6E−07	3.41E−08	2.58E−07	3.25E−07	3.75E−06	0	0
Max	7.77E−07	8.54E−08	6.19E−07	6.16E−07	7.76E−06	4.32E−07	4.13E−06
Average	3.9E−07	3.94E−08	2.96E−07	3.23E−07	3.51E−06	1.14E−07	6.32E−07
SD	2.42E−07	2.49E−08	1.86E−07	1.97E−07	2.55E−06	1.79E−07	1.54E−06

the risk levels of Cr at residential areas (B2), schools (B3), Olympic Park (B4) and rural countryside (B5) exceeded the limit of 10^{-6} for both men and women. FLA presented the maximum value for both adults and children, then followed by PYR > FLO > ANT. In HF days, the risk level of each functional area ranged in the order: rural countryside > inner suburban district > Olympic Park > city central > schools > ecological reserve > residential areas. The risk levels of DahA, BkF, BbF, IcdP, CHR and BaA were all under average risk acceptance and to some extent, BaP may had a potential risk to the environment.

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