Bull. Environ. Contam. Toxicol. (2005) 74:660–666

DOI: 10.1007/s00128-005-0634-y

Bulletin of Environmental Contamination and Toxicology

Seasonal Variation and Spatial Distribution of Polycyclic Aromatic Hydrocarbons in Atmospheric PM_{10} of Beijing, People's Republic of China

J. B. Zhou, T. G. Wang, Y. B. Huang, T. Mao, N. N. Zhong

Laboratory of Environmental Science and Geochemistry, College of Natural Resources and Information Technology, University of Petroleum, Beijing 102249, People's Republic of China

Received: 20 August 2004/Accepted: 18 January 2005

Polycyclic aromatic hydrocarbons(PAHs) are widespread harmful compounds formed primarily during incomplete combustion of carbon-containing materials. Several PAHs were confirmed by epidemiological studies to be animal mutagens and potential humans carcinogens(IARC, 1983), and exhibit a strong adsorption affinity on small particles(Gyula, 1998) because of their relative low vapour pressure and aromaticity. Furthermore, small particulate matter with an aerodynamic diameter less than 10μm(PM_{10}), which is considered to be represent thoracic fraction of ambient particles(Robert, 2003), has been given increasing attention in recent decades due to its potential adverse health impact(Dockery, 1994; BraunFahrlander, 1997). According to the report of Beijing Environmental Monitoring Center, the frequency of PM_{10} as primary air pollutant was approximately 85% in the period from 2000 to 2002, with the mean mass concentration of approximately 165μg/m^3. High atmospheric PM_{10} loading has been a persistent problem in Beijing.

The objective of this study is to investigate the seasonal variation and spatial distribution of PAHs at two different functional sites in Beijing. The preliminary human risk assessment associated with the PAHs level was also discussed.

MATERIALS AND METHODS

The sites chosen for the sampling of atmospheric PM_{10} were northern urban area and suburban area in Beijing. Urban sampling site is located in a mixed institutional, residential and commercial area, and suburban site in the campus of University of Petroleum. Samples of two sites were simultaneously acquired on the roof of two five-storey building(15m height). Particle samples were collected in the spring (28-30 April), summer(8-10 July), autumn (5-7 November) and winter(16-18 January) of 2003. The average air temperature of four sampling periods were 25℃, 33℃, 6℃,-3℃， respectively. Each sample was operated from 10:00 A.M. and lasted for 48h at a flow rate of 77.5L/min using a PM-10 air sampler fitted with quartz fiber filters. Before sampling, the quartz fiber filters were wrapped with aluminum foil and baked in a muffle furnace at 450℃ overnight.

Correspondence to: T. G. Wang

Airborne particles were extracted three times with redistilled dichloromethane under ultrasonic agitation for 20min each. The extracts were filtered through a filtration unit fitted with an annealed glass fiber filters to remove quartz fibers and particulate detritus. The extracts were then concentrated on a Büchi rotary evaporator(bath temperature≤30℃) to approximately 2ml. The concentrated samples were cleaned up and fractionated on a silica gel-alumina column. The column was packed by adding silica gel(activated at 180℃ for 12h), alumina (activated at 250℃ for 12h) and 1cm of anhydrous sodium sulfate (activated at 600℃ for 6h) in hexane-slurry in the given order. The samples were transferred to the column and eluted with hexane and hexane-dichloromethane(1:1) successively to give fractions enriched in alkanes and PAHs, respectively. The fractions containing PAHs were concentrated and blown down to 0.1ml using a gentle stream of dry nitrogen gas.

PAHs were measured by using an Finnigan SSQ710 gas chromatograph-mass spectrometer fitted with a fused silica capillary column(HP-5MS,30m,0.25mm i.d.,0.25μm film thickness).The GC-MS operating conditions were as follows: isothermal at 65℃ for 5min, temperature program 65℃-290℃ at 3℃min^{-1}, held isothermal at 290℃ for 20min and using helium as carrier gas. Data were acquired in the electron impact(EI) model(70ev), scanning from 35-500 mass unit.

Seven calibration standards containing 17 PAHs: naphthalene(Nap), acenaphthylene(Acy), acenaphthene(Ace), fluorene(Flu), phenanthrene(Phe), anthracene (Ant), fluoranthene(Flua), 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), dibenz[a,h]anthracene (DahA), benzo[g,h,i]perylene(BghiP), internal standard: hexamethylbenzene and surrogates compounds: naphthalene-d_8, acenaphthene-d_{10}, acenaphthene-d_{10}, chrysene-d_{12}, perylene-d_{12} were prepared to GC-MS analysis. The mean of the relative response factors for each target PAH and surrogate compounds were calculated from the calibration curve. 17 PAHs were quantified by the internal standard method.

Prior to ultrasonic extract of each sample, recovery tests were carried out by spiking of surrogates compounds. The average recovery were 43.6%,84.5%, 95.4%, 94.2%, 93.7% for naphthalene-d_8, acenaphthene-d_{10}, acenaphthene-d_{10}, chrysene-d_{12}, and perylene-d_{12} respectively. The relative standard deviation ranged from 3.91 to 9.35%. The method of detection limit(S/N=3) ranged from 0.004 to 0.023 ng/m^3. The relative standard deviation of target PAHs in four sample replicates were less than 9.86%. All solvents(Yili Chemical Co. Beijing, Analytical Pure) used were redistilled in glass appliance and aliquots were routinely checked as blanks. Field blanks were analyzed by the same procedure as the samples and ensured that there were no significant background interferences. No PAHs were detected.

RESULTS AND DISCUSSION

The concentrations of PAHs in atmospheric PM$_{10}$ during four seasons in Beijing were shown in Table1. Individual concentrations between 0.01 and 55.23 ng/m^3 were found and total 17 PAHs concentrations varied from 8.62 to 296.57 ng/m^3 with the average value of 107.49 ng/m^3. PAHs concentrations in urban site were 1.02～1.58 times higher than those measured in suburban site. The highest concentration was found for winter sample, which is followed by autumn and spring samples respectively, while the concentration of PAHs in summer is the lowest. Seasonal variation of PAHs concentrations showed a tendency that PAHs concentrations increased with decreasing ambient temperature of sampling periods. The total PAHs concentrations showed a seasonal variation (winter/summer) factor of 22.25 and 34.41 for suburban and urban sampling location, respectively, which suggested that coal combustion for domestic heating was the main reason for elevated concentration of airborne PAHs in winter.

Table 1. Concentration of PAHs determined in atmospheric PM$_{10}$ in Beijing (ng/m^3).

	spring		summer		autumn		winter	
PAHs name	urban	suburb	urban	suburb	urban	suburb	urban	suburb
Nap	0.18	0.29	0.79	0.15	1.28	0.01	0.51	0.37
Acy	0.05	0.09	0.05	0.01	0.45	0.17	2.95	0.92
Ace	0.02	0.04	0.05	0.35	0.17	0.04	0.17	0.08
Flu	0.16	0.35	0.42	0.01	2.46	0.75	3.10	1.73
Phe	1.15	2.30	1.89	0.48	10.45	6.38	28.14	16.48
Ant	0.13	0.27	0.15	0.06	1.42	1.06	5.88	3.01
Flua	3.05	4.98	2.34	0.61	12.79	15.79	55.23	29.30
Pyr	3.03	4.82	2.32	0.60	12.74	15.39	47.88	27.83
BaA	2.59	2.94	0.07	0.35	13.68	12.50	24.33	17.76
Chr	4.69	5.35	0.33	0.64	22.75	18.16	28.96	21.92
BbkF	12.78	11.55	0.06	1.28	6.26	8.46	30.46	22.60
BeP	5.91	5.23	0.06	1.00	10.05	6.16	11.94	9.68
BaP	5.30	4.51	0.03	0.58	5.58	5.40	14.30	11.11
IcdP	16.51	12.17	0.01	0.01	ND	1.55	19.70	10.03
DahA	2.09	1.47	ND*	0.10	ND	0.32	4.62	1.31
BghiP	18.48	15.02	0.05	2.20	11.92	6.46	18.40	14.06
∑PAHs	76.09	71.38	8.62	8.46	112.00	98.61	296.57	188.20

*ND: not detectable

Compared to PAHs level of other cities, the annual mean PAHs concentrations in this study was approximately two times higher than that in Macao(Qi, 2002) and one order of magnitude and even more higher than that in Malaysia(Omar,2002) and Italy(Caricchia, 1999). This shows serious PAHs pollution levels in Beijing.

The most potential carcinogen BaP concentrations in spring, summer, autumn samples were below the limit of China National Atmospheric Environmental Standard (10ng/m^3), and were 1.11 and 1.43 times higher than the standard in wintertime at two sampling sites, respectively. Concentration of BaP in this study, averaging 5.85 ng/m^3, was 3.1～4.2 times higher than levels reported for Rome(Menichini,1999), London(Brown,1996) and Chicago(Odabasi,1999), which showed a medium pollution level.

The results(Figure 1) of 17 normalized concentration showed lower molecular weight(2-3 rings)PAHs were less than 15% of the total mass(except in urban summer sample), while heavier PAHs(4 rings and more)showed three distribution patterns. Firstly(spring type), the PAHs normalized concentration increased with molecular size. Six-ring benzo(ghi)perylene, indeno(1,2,3-cd)pyrene, five-ring benzo(b+k)fluoranthene accounted for the majority of the total PAHs concentrations(Table 1), indicating that traffic emission was clearly a significant source of PAHs in spring. Secondly(summer type), the distribution characteristic of PAHs varied greatly in two sites. Four-ring fluoranthene, pyrene and three-ring phenanthrene dominated the total PAHs in urban sampling site, and BeP/BaP ratio was 2.17, resembling the PAH source fingerprints for diesel engines (Rogge,1993). These distribution characteristics were presumably related to emission of heavy-duty truck fueled by diesel in nighttime. Meanwhile, six-ring benzo(ghi)perylene, five-ring benzo(b+k)fluoranthene and benzo(e)pyrene were most abundant in suburban sample. Thirdly(autumn+winter type), four-ring PAHs were found to be most aboundant in which fluoranthene, pyrene, benzo(a) anthracene and chrysene accounted for more than 50% of the total PAHs. It was likely ascribed to the contribution from mixed source of coal combustion and vehicles exhaust.

To assess human health risk associated with inhalatory exposure to PAHs in airborne particles, toxic equivalency factors(TEFs) proposed by Nisbet (1992) was introduced in this paper. The adjusted concentrations of individual PAHs were calculated in terms of benzo(a)pyrene equivalents. The results of these calculations were presented in Table 2. Fluoranthene, pyrene, benzo[b] fluoranthene and benzo[k]fluoranthene which dominate nearly all samples obviously play only a minor role in the carcinogenicity of the PAH mixture. Based on the proposed TEFs value, however, the contribution of the carcinogenic potency of BaP alone is in the range of 49-70% of the activity of the different PAH mixtures in air. Average total concentration of 11.474 ng BaP-equivalents /m^3 was calculated for urban area, while the suburban area was calculated to be 8.987 ng BaP-equivalents/m^3. These values were approximately 2～5 times higher than that of Copenhagen(Nielsen, 1996) and Nagasaki (Wada,2001). The US EPA lifetime unit risk value for BaP was adopted in this study, which predicts a risk of maximally one excess lung cancer in one million individual inhaling air with 0.3 ng BaP/m^3 for a lifetime. Therefore, the average BaP-equivalent concentration obtained for the urban area would imply an excess in lung cancers of 38.2 in one million individuals exposed in the open air for a lifetime. The corresponding value for suburban area would be 30.0 cases among one million

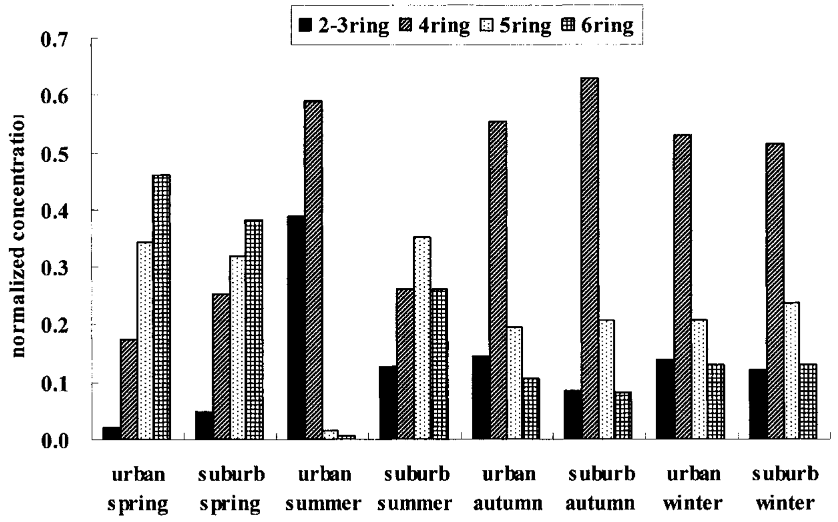

Figure 1. Normalized concentrations of PAHs with different rings in atmospheric PM$_{10}$.

Table 2. Toxic equivalency factors(TEFs) adjusted concentration of PAHs in Beijing(ng/m^3).

		spring		summer		autumn		winter	
PAHs name	TEFs	urban	suburb	urban	suburb	urban	suburb	urban	suburb
Nap	0.001	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Acy	0.001	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ace	0.001	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Flu	0.001	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Phe	0.001	<0.01	<0.01	<0.01	<0.01	0.01	0.01	0.03	0.02
Ant	0.01	<0.01	<0.01	<0.01	<0.01	0.01	0.01	0.06	0.03
Flua	0.001	<0.01	<0.01	<0.01	<0.01	0.01	0.02	0.06	0.03
Pyr	0.001	<0.01	<0.01	<0.01	<0.01	0.01	0.02	0.05	0.03
BaA	0.1	0.26	0.29	0.01	0.04	1.37	1.25	2.43	1.78
Chr	0.01	0.05	0.05	<0.01	0.01	0.23	0.18	0.29	0.22
BbkF*	0.1	1.28	1.15	0.01	0.13	0.63	0.85	3.05	2.26
BaP	1	5.30	4.51	0.03	0.58	5.58	5.40	14.30	11.11
IcdP	0.1	1.65	1.22	<0.01	<0.01	<0.01	0.16	1.97	1.00
DahA	1	2.09	1.47	<0.01	0.10	<0.01	0.32	4.62	1.31
BghiP	0.01	0.18	0.15	<0.01	0.02	0.12	0.06	0.18	0.14
∑PAHs		10.82	8.87	0.05	0.88	7.98	8.27	27.05	17.93
BaP/TotalPAHs		0.49	0.51	0.50	0.66	0.70	0.65	0.53	0.62

*BbkF: BbF + BkF

individuals exposed in the open air. It should be noted that the risk assessment was not very precise because many potential carcinogenic PAHs were not covered due to inadequate epidemiological findings. In addition, the carcinogenic effect of PAHs mixture of airborne particles humans are exposed to is not just sum of contributions from each single PAH. Nevertheless, high concentration BaP-equivalents in Beijing would pose a potential health threat to humans and must be seriously taken into account by relevant administrative authority.

Acknowledgments. This research was supported by doctoral funds from Ministry of Education, P. R. China, Grant No. 20030425007. We would like to thank Zhang Yi and Lei Chunsheng for their assistance in air sampling and Prof. Zhang Xiaoshan of Research Center for Eco-Environment Sciences, Chinese Academy of Sciences for his support during the study.

REFERENCES

BraunFahrlander C, Vuille JC, Sennhauser FH, Neu U, Kunzle T, Grize L, Gassner M, Minder C, Schindler C, Varonier HS, Wuthrich B(1997) Respiratory health and long- term exposure to air pollutants in Swiss school children. American Journal of Respiratory and Critical Care Medicine 155: 1042-1049.

Brown JR, Field RA, Goldstone ME (1996) Polycyclic aromatic hydrocarbons in central London air during 1991 and 1992. Sci Tot Environ 177: 73-84.

Caricchia AM, Chiavarini S, Pezza M (1999) Polycyclic aromatic hydrocarbons in the urban atmospheric particulate matter in the city of Naples(Italy). Atmos Environ 33: 3731-3738.

Dockery, DW, Pope CA (1994) Acute respiratory effects of particulate air pollution. Ann Rev Pub Health 15: 107-132.

Gyula K, Zita V P, Gabor R, Jozsef H (1998) Distribution of polycyclic aromatic hydrocarbons on atmospheric aerosol particles of different sizes. Atmos Res 46: 253-261.

IARC (1983) IARC Monographs on the evaluation of the carcinogenic risk of chemicals to humans. International Agency for Research on Cancer, Lyon, France.

Menichini E, Monfredini F, Merli F (1999) The temporal variability of the profile of carcinogenic polycyclic aromatic hydrocarbons in urban air: a study in a medium traffic area in Rome, 1993-1998. Atmos Environ 33: 3739-3750.

Nielsen T, JØrgensen HE, Larsen JC (1996) City air pollution of polycyclic aromatic hydrocarbons and other mutagens: occurrence, sources and health effects. Sci Tot Environ 189/190:41-49.

Nisbet C, LaGoy P (1992) Toxic equivalency factors(TEFs) for polycyclic aromati hydrocarbons (PAHs). Reg Toxicol Pharmacol 16: 290-300.

Odabasi M, Vardar N, Sofuoglu A, Tasdemir Y, Holsen T M (1999) Polycyclic aromatic hydrocarbons(PAHs) in Chicago air. Sci Tot Environ 227: 57-67.

Omar NYMJ, Abas MRB, Ketuly KA, Tahir NM (2002) Concentrations of PAHs in atmospheric particles and roadside soil particles collected in Kuala Lumpur, Malaysia. Atmos Environ 36: 247-254.

Qi S H, Sheng G Y, Fu J M, Wang Z S, Min Y S (2002) Source apportionment experiment of polycyclic aromatic hydrocarbons(PAHs) in aerosols in Macao. China Environ Sci 22: 118-122 (in Chinese).

Robert G, Brigitte B (2003) Characterising seasonal variations and spatial distribution of ambient PM10 and PM2.5 concentrations based on long-term Swiss monitoring data. Atmos Environ 37: 2571-2580.

Rogge W F, Hildemann L M,Mazurek M A, Cass G R, Simoneit B R T (1993) Sources of fine aerosol. 2.Noncatalyst and catalyst-eqipped automobiles and heavy duty diesel trucks. Environ Sci Technol 27: 636-651.

Wada M, Kido H, Kishikawa N, Tou T, Tanaka M, Tsubokura J, Shironita M, Matsui M, Kuroda N, Nakashima k (2001) Assessment of air pollution in Nagasaki city: determination of polycyclic aromatic hydrocarbons and their nitrated derivatives, and some metals. Environ Pollut 115: 139-147.