Supporting Information for

The influence of the Clean Air Actions on the health risk of atmospheric polycyclic aromatic hydrocarbons

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S1. Text

Text S1. Sampling and analytical procedure of PAHs

The air samples were collected at an urban site (latitude: 45°45′28″ N; longitude: 126°40′49″ E) in Harbin, the capital city of Heilongjiang Province in northeastern China. Normally, almost weekly air samples were collected by a high-volume air sampler (TE-1000, Tisch Environmental, Ohio, USA) with an air flow of 0.24 std m^3/min for 24 h from June 2014 to May 2019. In total, 194 pairs of gas phase and particle phase samples (total suspended particles) were collected in the long-term monitoring program. The sampling and analytical procedures were modified from our previous studies (Ma et al. 2010, Ma et al. 2018). In brief, gas phase and particle phase samples were collected on polyurethane foam (PUF) plugs and glass fiber filters (GFFs), respectively. After sampling, GFFs and PUFs were spiked with surrogates and then extracted and purified by the Soxhlet extraction method and active silica gel column, respectively.

In total, 15 priority PAHs were analyzed by an Agilent 6890N GC coupled with an Agilent 5973 mass spectrometer detector: acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fluo), pyrene (Pyr), BaA, benz[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenz[a,h]anthracene (DahA), indeno[l,2,3-cd]pyrene (IcdP), and benzo[g,h,i]perylene (BghiP). Separation was achieved using 30m × 0.25 mm × 0.25 μm HP-5MS capillary column (Agilent Co., USA) in selected ion monitoring (SIM) mode. The quantitative ions and the qualitative ions for PAHs and the PAH surrogates were shown in Table S1. A 2.0 μL volume of sample was injected in the splitless mode. The column temperature programs were used as follows: held at 90 °C for 1 min, then raised from 90 °C to 180

51 °C with 10 °C /min, held for 1 min, from 180 °C to 280 °C at 3 °C/min, held for 20
52 min.
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Text S2. Quality assurance/quality control (QA/QC)

The field blank was confirmed, with only trace levels of some low ring PAHs being detected by loading a precleaned PUF plug and GFF into the sampler for 1 min with no air drawing through for each month. For each batch of real samples, one lab blank was added to check the background interference during the experiment. The results indicated that only trace levels of low molecular weight PAHs could be detected in laboratory blanks. The average recoveries of the three surrogates (Flu-D10, Pyr-D10, and Perylene-D12) were 80%, 87%, and 69% for PUF samples and 75%, 92%, and 80% for GFF samples, respectively. The final reported concentrations were surrogate corrected but not blank corrected. The instrument and method detection limits ranged from 0.10 ng/mL to 0.73 ng/mL and from 0.0180 ng/m^3 to 0.0774 ng/m^3, respectively.

S2. Tables

Table S1. Toxic equivalency factors (TEFs) and Halving time for the 15 PAHs

PAHs	Abb.[a]	TEFs	Halving time[b]	Quantitative ion	Qualitative ion
acenaphthylene	Acy	0.001	4.78 ± 0.963	152.1	151.1
acenaphthene	Ace	0.001	3.03 ± 0.352	153.1	154.1
fluorene	Flu	0.001	3.10 ± 0.328	166.1	165.1
phenanthrene	Phe	0.001	3.09 ± 0.323	178.1	176.1
anthracene	Ant	0.01	2.27 ± 0.258	178.1	176.1
fluoranthene	Fluo	0.001	3.62 ± 0.510	202.1	200.1
pyrene	Pyr	0.001	3.74 ± 0.550	202.1	200.1
benzo[a]anthracene	BaA	0.1	3.17 ± 0.439	228	226
chrysene	Chr	0.01	3.05 ± 0.371	228	226
benzo[b]fluoranthene	BbF	0.1	5.03 ± 0.901	252	250
benzo[k]fluoranthene	BkF	0.1	3.69 ± 0.533	252	250
benzo[a]pyrene	BaP	1	3.92 ± 0.605	252	250
indeo[1,2,3-cd]pyrene	IcdP	0.1	4.18 ± 0.659	276	274
dibenzo[a,h]anthracene	DahA	1	3.20 ± 0.421	278	276
benzo[g.h,j]perylene	BghiP	0.01	3.56 ± 0.483	276	274

Note: a, Abbreviation; b Halving time for the concentrations of 15 PAHs in the bulk air (particle plus gas phase) is cited from study[1].

Table S2. The exposure factors for daily exposure dose for different age groups.

Parameter	Unit		Distribution	Children (1-11)	Adolescent (12-17)	Adult (18-70)
IR[a]	$m^3\ day^{-1}$	mean (95%)	lognormal	8.9 (10.2)	13.9 (18.7)	16.7 (21.1)
EF[b]	dimensionless	mean (95%)	lognormal	0.0972 (0.25)	0.0618 (0.101)	0.126 (0.333)
BW[a]	kg	mean (95%)	normal	19.7 (25.8)	50.9 (71.1)	67.2 (88.2)
SA[a]	m^2	mean (95%)	normal	0.148 (0.174)	0.230 (0.284)	0.209 (0.246)
AF[d]	$mg\ cm^{-2}\ event^{-1}$	geomean (geosd)	lognormal	0.04 (3.41)	0.04 (3.41)	0.02 (2.67)
EV[d]	$events\ day^{-1}$	-	-	1	1	1
ABS_d[d]	dimensionless	geomean (geosd)	lognormal	0.13 (1.26)	0.13 (1.26)	0.13 (1.26)
CSF_i[e]	$kg\ day\ mg^{-1}$	geomean (geosd)	lognormal	3.14 (1.80)	3.14 (1.80)	3.14 (1.80)
CSF_d[e]	$kg\ day\ mg^{-1}$	-	-	37.47	37.47	37.47
$ADAF$	dimensionless	-	-	1-2 years old: 10; 3-11 years old: 3	12-15 years old: 3; 16-17 years old: 1	1

a, the parameters for children and adolescents were the statistical data cited from the Chinese Exposure Factors Handbook (Children)[2]. The parameters for adults were the statistical data cited from Exposure Factors Handbook of Chinese Population (Adults)[3].

b, the values of EF were calculated from the outdoor time (T, min) in a day using $EF = T/60/24$[2, 3].

c, the data were calculated from the different percentage of the total body surface area from the handbooks[2, 3].

d, the data were cited from the Risk Assessment Guidance for Superfund that developed by the U.S. Environmental Protection Agency (EPA)[4].

e, CSF_i and CSF_d were the cancer slope factors for inhalation exposure and dermal contact, respectively[5].

Table S3. Statistical summary of $\sum BaP_{eq}$ concentration (ng m^{-3}) of 15 atmospheric PAHs in the particle phase, gas phase, and total phase in Harbin from June 2014 to May 2019.

Period	Mean	SD	Media	Range (min-max)	Range (25%-75%)
			Particle phase		
2014.6~2015.5	7.99	12.2	3.06	0.450 - 43.4	0.741 - 7.37
2015.6~2016.5	9.39	15.6	1.45	0.244 - 59.5	0.525 - 12.3
2016.6~2017.5	9.47	12.7	1.44	0.169 - 54.0	0.698 - 16.2
2017.6~2018.5	7.71	12.1	1.84	0.211 - 42.2	0.612 - 10.3
2018.6~2019.5	3.46	3.85	1.38	0.123 - 13.2	0.509 - 5.63
All	7.67	12.1	1.84	0.123 - 59.5	0.654 - 9.26
			Gas phase		
2014.6~2015.5	0.210	0.163	0.150	0.0443 - 0.712	0.109 - 0.255
2015.6~2016.5	0.214	0.181	0.146	0.0330 - 0.885	0.0845 - 0.312
2016.6~2017.5	0.129	0.108	0.0970	0.0473 - 0.594	0.0659 - 0.140
2017.6~2018.5	0.165	0.179	0.0906	0.0208 - 0.809	0.0535 - 0.203
2018.6~2019.5	0.0800	0.0624	0.0610	0.0167 - 0.353	0.0388 - 0.110
All	0.164	0.157	0.115	0.0167 - 0.885	0.0646 - 0.196
			Total phase		
2014.6~2015.5	8.20	12.3	3.16	0.520 - 44.1	0.946 - 7.53
2015.6~2016.5	9.61	15.7	1.57	0.327 - 60.0	0.634 - 12.7
2016.6~2017.5	9.60	12.8	1.51	0.217 - 54.7	0.800 - 16.3
2017.6~2018.5	7.88	12.2	2.01	0.292 - 42.5	0.695 - 10.3
2018.6~2019.5	3.54	3.90	1.42	0.147 - 13.4	0.570 - 5.74
All	7.83	12.2	2.02	0.147 - 60.0	0.736 - 9.43

References

(1) Zhu, Fu-Jie; Ma, Wan-Li; Hu, Peng-Tuan; Zhang, Zi-Feng; Li, Yi-Fan. Temporal trends of atmospheric PAHs: Implications for the influence of the clean air action. *Journal of Cleaner Production* 2021**,** *296*, 126494. DOI: 10.1016/j.jclepro.2021.126494.

(2) Duan, Xiaoli; Zhao, Xiuge; Wang, Beibei; Chen, Yiting; Cao, Suzhen. In *Highlights of the Chinese Exposure Factors Handbook (Children)*, Academic Press, 2016. https://www.researchgate.net/publication/311607926_Highlight_of_Chinese_Children's_Exposure_Factors_Handbook_zhongguoertongbaolucanshushoucegaiyao#fullTextFileContent.

(3) Duan, Xiaoli; Zhao, Xiuge; Wang, Beibei; Chen, Yiting; Cao, Suzhen. In *Highlights of the Chinese Exposure Factors Handbook (Adults)*, Academic Press, 2015; p vii. DOI: 10.1016/B978-0-12-803125-4.00005-5.

(4) USEPA. *Risk Assessment Guidance for Superfund, Human Health Evaluation Manual, Pt E, Supplemental Guidance for Dermal Risk Assessment.*; 2004.

(5) Liao, ChungMin; Chiang, KuoChih. Probabilistic risk assessment for personal exposure to carcinogenic polycyclic aromatic hydrocarbons in Taiwanese temples. *Chemosphere* 2006**,** *63* (9), 1610-1619. DOI: 10.1016/j.chemosphere.2005.08.051.