

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30

Supporting Information for

**Phthalate Esters in Indoor Window Films in a Northeastern
Chinese Urban Center: Film Growth and Implications for
Human Exposure**

Chun-Yan Huo^{†,‡}, Li-Yan Liu^{*†}, Zi-Feng Zhang[†], Wan-Li Ma[†], Wei-Wei Song[†],
Hai-Ling Li[†], Wen-Long Li[†], Kurunthachalam Kannan[§], Yong-Kai Wu[†], Ya-Meng
Han[†], Zhi-Xiang Peng[†], Yi-Fan Li^{*†,‡,¶}

[†] International Joint Research Center for Persistent Toxic Substances (IJRC-PTS),
State Key Laboratory of Urban Water Resource and Environment, School of
Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin
150090, China

[‡] School of Environmental Science, Liaoning University, Shenyang 110036, China

[§] Wadsworth Center, New York State Department of Health, Department of
Environmental Health Sciences, School of Public Health, State University of New
York at Albany, Empire State Plaza, P.O. Box 509, Albany, New York 12201-0509,
United States

[¶] IJRC-PTS-NA, Toronto, M2N 6X9, Canada

*Corresponding authors.
Tel. +86-451-8628-9130; Fax: +86-451-8628-9130.
Email address: ijrc_pts_paper@yahoo.com (L.Y. Liu; Y. F. Li)

For submission to: Environmental Science & Technology

Pages: 15

Figures: 7

Tables: 5

Contents

32	S1. Supplementary Tables	1
33	Table S1. The results of QA/QC (mean \pm standard deviation) in the present study.	1
34	Table S2. The converted median concentrations of DiBP, DBP and DEHP (in ng/m^3 air) in	
35	indoor air in this study and monitoring data from various studies around the world.....	2
36	Table S3. Parameters for the equations to calculate the daily exposure dose (DED) for DiBP,	
37	DBP and DEHP via indoor air inhalation (DED_{air}), film ingestion ($\text{DED}_{\text{film-i}}$) film dermal	
38	absorption ($\text{DED}_{\text{film-da}}$) for teenagers and adults ⁹	3
39	Table S4. Summary of PAE concentrations (in $\mu\text{g}/\text{g}$ film) in the glass window film samples in	
40	winter and summer.	4
41	Table S5. Summary of the median and 25 th –75 th percentile values for DED_{air} (in	
42	$\mu\text{g}/\text{kg-bw}/\text{day}$), $\text{DED}_{\text{film-i}}$ (in $\mu\text{g}/\text{kg-bw}/\text{day}$), $\text{DED}_{\text{film-da}}$ (in $\mu\text{g}/\text{kg-bw}/\text{day}$), DEDt (in	
43	$\mu\text{g}/\text{kg-bw}/\text{day}$) and HQ for the summer and winter samples.....	5
44	S2. Supplementary Figures	6
45	Figure S1. The location of sampling sites in Harbin City, Heilongjiang Province, China.	6
46	Figure S2. Blank proportion (%) over time calculated by dividing the mean blank values by	
47	the values detected in film samples collected over time.	7
48	Figure S3. LogK_{OA} as functions of temperature.....	8
49	Figure S4. Correlation analysis of natural logarithm PAE concentrations (in ng/m^2) in	
50	window film samples collected in winter (a) and summer (b).	9
51	Figure S5. Loading plots (a) and score plots (b) of PCA for PAEs in the window film	
52	samples. For the abbreviation in the score plots, W means winter samples; S means	
53	summer samples.	10
54	Figure S6. Comparison of PAE concentrations (ng/m^2) in the building A and B with different	
55	sampling methods.....	11
56	Figure S7. The PAE concentrations (in $\mu\text{g}/\text{g}$) in the glass window films as a function of	
57	growth days in winter (a) and summer (b).	12
58	References	13
59		
60		
61		
62		
63		
64		
65		
66		
67		

68 **S1.Supplementary Tables**69 **Table S1.** The results of QA/QC (mean \pm standard deviation) in the present study.

	DMP-D ₄	DEP-D ₄	DiBP-D ₄	DBP-D ₄	BBP-D ₄	DEHP-D ₄
Recoveries in method blank (n = 16) ^a	70 \pm 11%	70 \pm 12%	71 \pm 8.4%	74 \pm 9.1%	84 \pm 7.1%	74 \pm 5.0%
Recoveries in method spiked (n = 16) ^a	71 \pm 9.2%	71 \pm 10%	73 \pm 7.7%	74 \pm 7.5%	86 \pm 8.4%	77 \pm 5.9%
Recoveries in film samples (n = 64) ^a	70 \pm 5.9%	75 \pm 5.2%	76 \pm 4.3%	79 \pm 5.0%	85 \pm 8.5%	81 \pm 8.7%
	DMP	DEP	DiBP	DBP	BBP	DEHP
Values in method blanks (n = 16) ^{b, c}	27 \pm 6.0 ng/m ²	5.0 \pm 2.2 ng/m ²	42 \pm 19 ng/m ²	57 \pm 11 ng/m ²	2.0 \pm 2.0 ng/m ²	57 \pm 12 ng/m ²
MDLs ^d	43 ng/m ²	11 ng/m ²	99 ng/m ²	90 ng/m ²	8.0 ng/m ²	93 ng/m ²
Recoveries in method spiked (n = 16) ^{c,e}	116 \pm 11%	108 \pm 13%	113 \pm 10%	116 \pm 7.8%	96 \pm 7.5%	114 \pm 11%
Values in film samples before corrected by blank (n = 64) ^c	230 \pm 130 ng/m ²	29 \pm 14 ng/m ²	520 \pm 290 ng/m ²	1700 \pm 840 ng/m ²	57 \pm 67 ng/m ²	6900 \pm 5900 ng/m ²
Values in film samples after corrected by blank (n = 64) ^{c,f}	170 \pm 120 ng/m ²	19 \pm 14 ng/m ²	410 \pm 300 ng/m ²	1500 \pm 840 ng/m ²	52 \pm 66 ng/m ²	6800 \pm 5900 ng/m ²

^a: The mass of each PAE-D₄ that was loaded was 100 ng.
^b: Values in method blanks were divided by the sampling area of window for each of batch of real samples.
^c: All results adjusted by dividing by the recoveries of deuterated spikes.
^d: The method detection limits (MDLs) was calculated by the mean blank values plus three times the standard deviation.
^e: The mass of each PAE that was loaded was 500 ng.
^f: Concentrations of each PAE were subtracted from the mean blank values of each batch of two blank samples.

70

71

72 **Table S2.** The converted median concentrations of DiBP, DBP and DEHP (in ng/m³
73 air) in indoor air in this study and monitoring data from various studies around the
74 world

Country	Year	DiBP	DBP	DEHP	References
China	2014	280	660	200	This study
China	2015	350	1600	140	This study
USA	2014-2015	na ^a	na ^a	300	Bi et al., 2015 ¹
China	2013	na ^a	1100	1100	Song et al., 2015 ²
China	2011-2012	na ^a	1939	2437	Pei et al., 2013 ³
Sweden	na ^a	270 ^b	850 ^b	200 ^b	Bergh et al., 2011 ⁴
Sweden	na ^a	190 ^c	600 ^c	240 ^c	Bergh et al., 2011 ⁴
Sweden	na ^a	230 ^d	550 ^d	100 ^d	Bergh et al., 2011 ⁴
USA	2006	130	140	68	Rudel et al., 2010 ⁵
Japan	2006-2007	75	200	147	Kanazawa et al., 2010 ⁶
Germany	2000-2001	na ^a	1083	156	Fromme et al., 2004 ⁷
USA	1999-2001	61	220	77	Rudel et al., 2003 ⁸

na^a: not available.

^b: Samples collected at private homes.

^c: Samples collected at workplaces.

^d: Samples collected at day care centers.

75

76

77 **Table S3.** Parameters for the equations to calculate the daily exposure dose (DED) for
 78 DiBP, DBP and DEHP via indoor air inhalation (DED_{air}), film ingestion (DED_{film-i})
 79 film dermal absorption (DED_{film-da}) for teenagers and adults⁹

Category	Units	Teenagers (Age: 12-19 ^{9, 10})	Adults (Age ≥ 20 ^{9, 10})
IR	m ³ /day	14	13.3
BW	kg	52 ^{9, 10}	62.9 ¹¹
BSA ⁹	cm ²	3692	4615
FAS ⁹	mg/cm/day	0.096	0.096
AF ^{9, 12}	-	0.03	0.03
IEF ^{9, 13}	-	0.875	0.875
DIR ^{9, 10}	(g/day)	0.05	0.05

80

81 **Table S4.** Summary of PAE concentrations (in $\mu\text{g/g}$ film) in the glass window film
 82 samples in winter and summer.

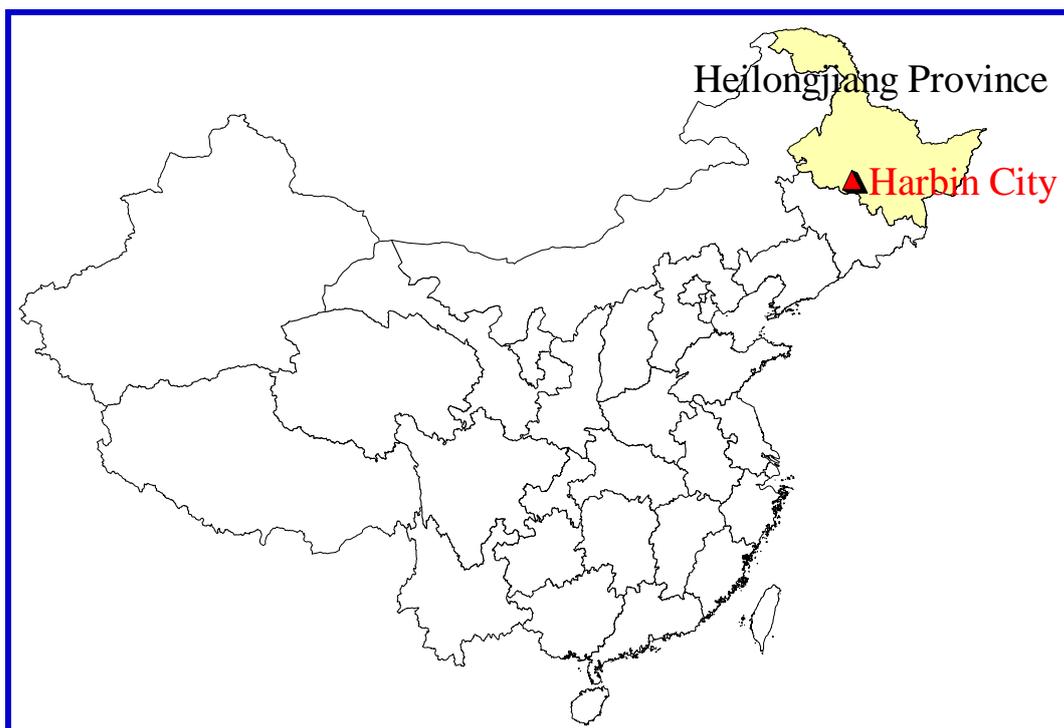
	Winter			Summer		
	25 th -75 th percentile	Geo. Mean	Median	25 th -75 th percentile	Geo. Mean	Median
DMP	23-48	23	27	9.5-29	18	12
DEP	2.2-5.9	2.1	2.4	1.2-3.0	2.0	1.7
DiBP	60-170	110	110	23-41	32	32
DBP	220-460	320	320	120-270	170	180
BBP	6.0-18	11	12	2.6-4.7	3.2	3.6
DEHP	990-2200	1700	1500	340-630	460	440
$\Sigma_6\text{PAEs}$	1300-2800	2200	2000	510-850	700	650

83

84 **Table S5.** Summary of the median and 25th–75th percentile values for DED_{air} (in µg/kg-bw/day), DED_{film-i} (in µg/kg-bw/day), DED_{film-da} (in
85 µg/kg-bw/day), DED_t (in µg/kg-bw/day) and HQ for the summer and winter samples.

	Season	DiBP	DBP	DEHP	Total	DiBP	DBP	DEHP	Total
Teenagers					Adults				
DED _{air}	winter	0.065 (0.031-0.11)	0.16 (0.089-0.43)	0.066 (0.058-0.11)	0.34 (0.18-0.65)	0.051 (0.024-0.089)	0.12 (0.07-0.34)	0.052 (0.045-0.086)	0.27 (0.14-0.51)
DED _{air}	summer	0.083 (0.051-0.094)	0.38 (0.27-0.67)	0.032 (0.024-0.039)	0.49 (0.35-0.79)	0.065 (0.040-0.074)	0.30 (0.22-0.53)	0.025 (0.019-0.031)	0.38 (0.28-0.62)
DED _{film-i}	winter	0.095 (0.051-0.15)	0.27 (0.18-0.38)	1.2 (0.83-1.9)	1.7 (1.0-2.4)	0.079 (0.042-0.12)	0.23 (0.15-0.32)	1.0 (0.70-1.5)	1.4 (0.87-1.9)
DED _{film-i}	summer	0.027 (0.019-0.034)	0.15 (0.10-0.22)	0.37 (0.29-0.53)	0.54 (0.41-0.69)	0.022 (0.016-0.028)	0.13 (0.085-0.19)	0.31 (0.24-0.44)	0.45 (0.34-0.57)
DED _{film-da}	winter	0.020 (0.011-0.031)	0.058 (0.039-0.081)	0.26 (0.18-0.39)	0.35 (0.22-0.50)	0.021 (0.011-0.032)	0.060 (0.040-0.084)	0.27 (0.18-0.41)	0.37 (0.23-0.52)
DED _{film-da}	summer	0.006 (0.004-0.007)	0.033 (0.022-0.048)	0.078 (0.061-0.11)	0.12 (0.087-0.15)	0.006 (0.004-0.008)	0.034 (0.023-0.049)	0.081 (0.063-0.12)	0.12 (0.090-0.15)
DED _t	winter	0.19 (0.13-0.28)	0.55 (0.32-0.87)	1.6 (1.1-2.3)	2.3 (1.7-3.3)	0.16 (0.11-0.23)	0.46 (0.27-0.72)	1.4 (0.92-2.0)	2.0 (1.5-2.8)
DED _t	summer	0.11 (0.09-0.12)	0.62 (0.43-0.96)	0.50 (0.37-0.70)	1.3 (0.91-1.56)	0.087 (0.074-0.10)	0.49 (0.35-0.77)	0.42 (0.32-0.60)	1.1 (0.76-1.3)
HQ	winter	0.019 (0.013-0.028)	0.055 (0.031-0.087)	0.031 (0.021-0.047)	0.11 (0.068-0.17)	0.016 (0.011-0.023)	0.046 (0.027-0.072)	0.027 (0.018-0.040)	0.095 (0.058-0.14)
HQ	summer	0.011 (0.009-0.012)	0.062 (0.043-0.096)	0.010 (0.008-0.014)	0.087 (0.061-0.12)	0.008 (0.007-0.010)	0.044 (0.035-0.74)	0.008 (0.006-0.012)	0.071 (0.049-0.094)

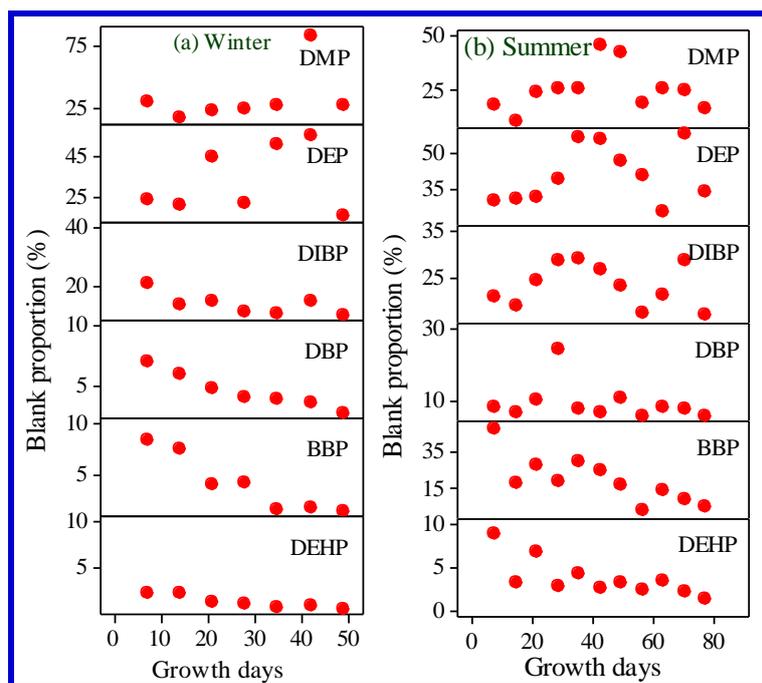
86 **S2.Supplementary Figures**



87

88 **Figure S1.** The location of sampling sites in Harbin City, Heilongjiang Province,
89 China.

90



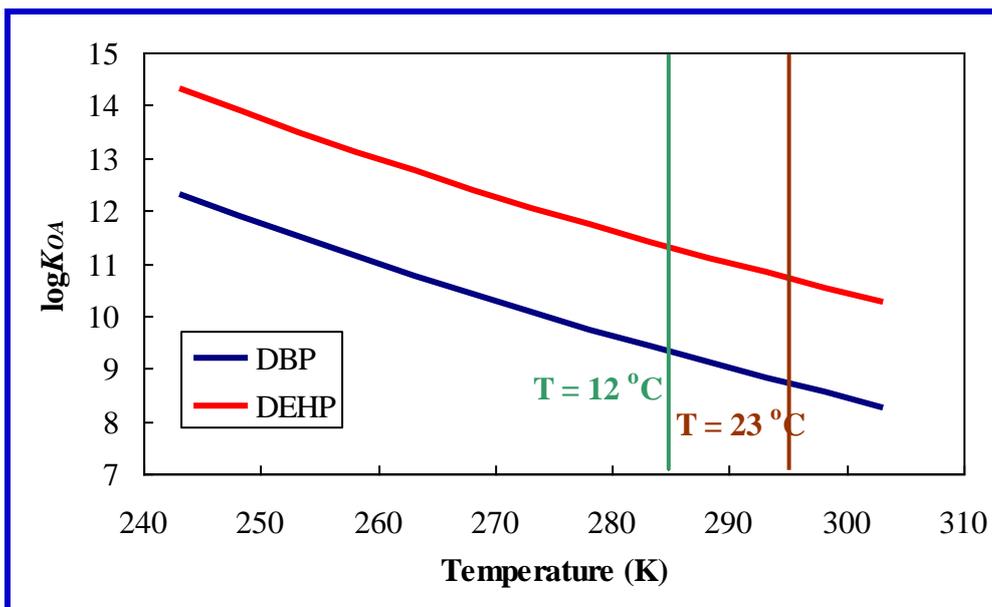
91

92 **Figure S2.** Blank proportion (%) over time calculated by dividing the mean blank
 93 values by the values detected in film samples collected over time.

94

95 Proportions of PAEs in the blank samples over time suggested that, in general, the
 96 precision of DBP, DiBP, BBP and DEHP increased along with the sampling time (see
 97 Figure S2). The levels of DBP, DiBP, BBP and DEHP in blanks were generally less
 98 than 30% of the levels in film samples. The precision of DEP and DMP was not as
 99 good as the other four PAEs. The PAE concentrations in each batch of samples were
 100 firstly subtracted from the mean blank values of the corresponding batch of samples.
 101 If the subtracted concentrations were lower than three times the standard deviation of
 102 the blank values, the PAE concentrations in the films were then treated as 1/2 of
 103 MDLs. That is, the concentrations below mean blank values plus three times the
 104 standard deviation (MDLs) were treated as half the value of MDLs for statistical
 105 analysis.

106



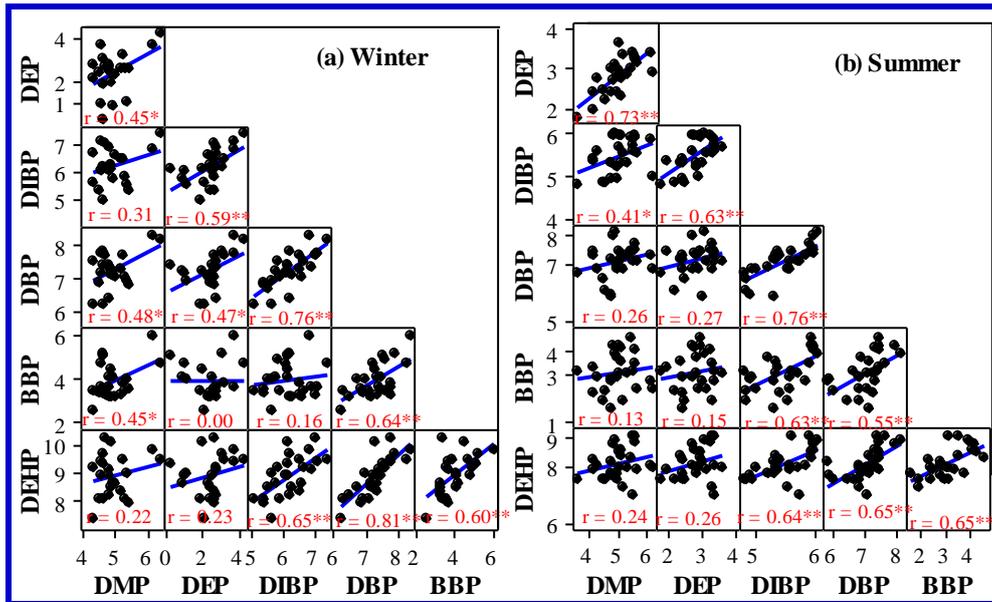
107

108

Figure S3. $\log K_{OA}$ as functions of temperature.

109

110

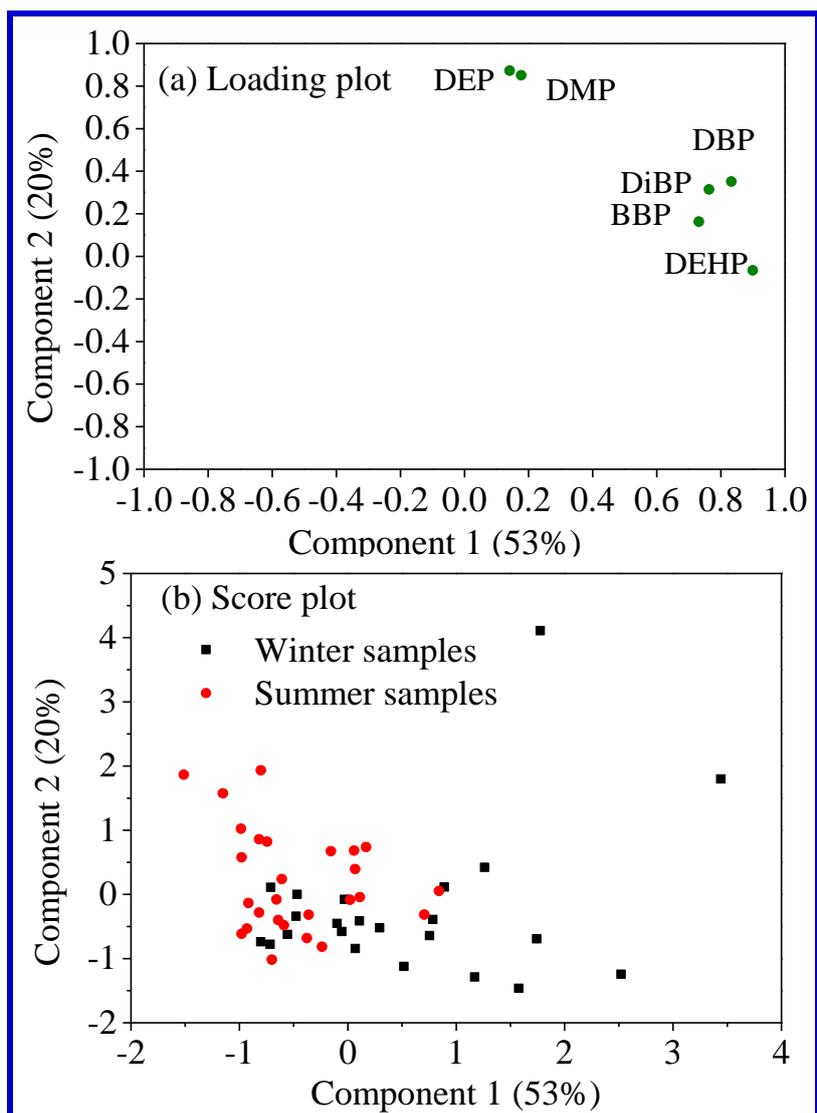


111

112 **Figure S4.** Correlation analysis of natural logarithm PAE concentrations (in ng/m²) in
 113 window film samples collected in winter (a) and summer (b).

114 The correlation coefficients are given in red color in the scatterplot matrices. One star
 115 (*) and two stars (**) mean correlation is significant at the 0.05 and 0.01 level
 116 (2-tailed), respectively.

117



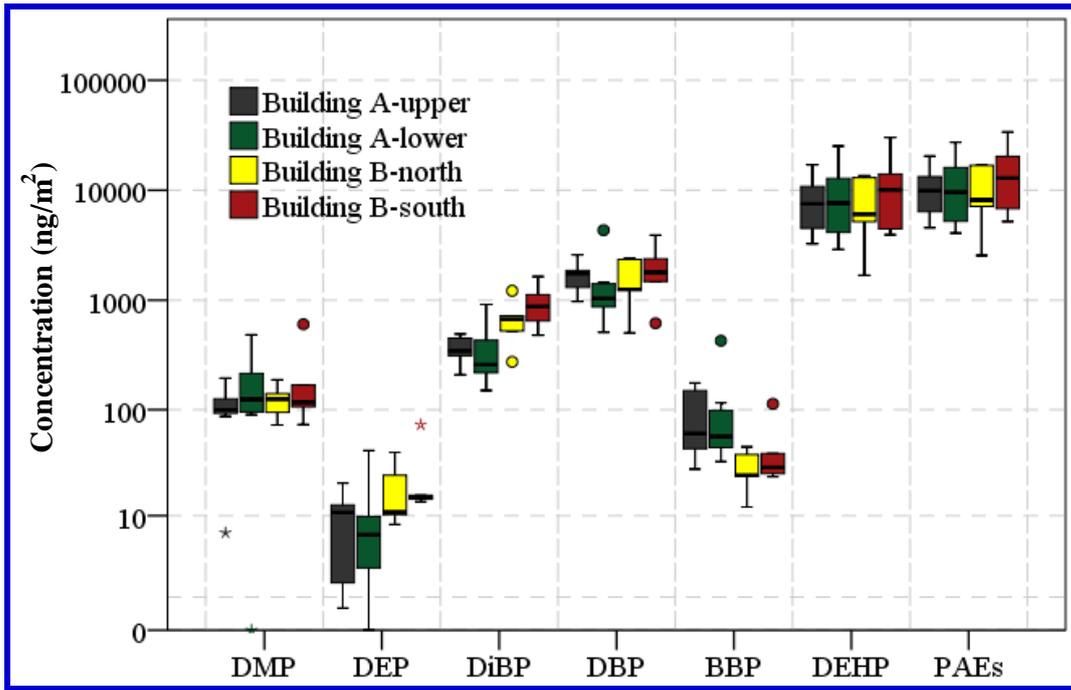
118

119 **Figure S5.** Loading plots (a) and score plots (b) of PCA for PAEs in the window film

120 samples. For the abbreviation in the score plots, W means winter samples; S means

121 summer samples.

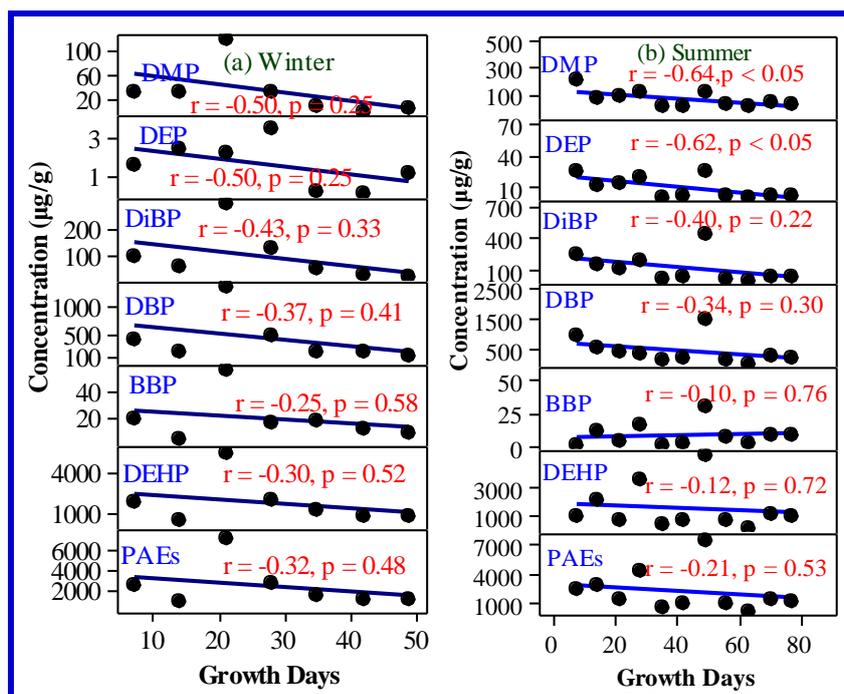
122



123

124 **Figure S6.** Comparison of PAE concentrations (ng/m²) in the building A and B with
 125 different sampling methods.

126



127

128 **Figure S7.** The PAE concentrations (in $\mu\text{g/g}$) in the glass window films as a function

129 of growth days in winter (a) and summer (b).

130

131

132

References

- 134 (1) Bi, C. Y.; Liang, Y. R.; Xu, Y., Fate and Transport of Phthalates in Indoor Environments and the
135 Influence of Temperature: A Case Study in a Test House. *Environ. Sci. Technol.* **2015**, *49*, (16),
136 9674-9681.
- 137 (2) Song, M.; Chi, C. C.; Guo, M.; Wang, X. Q.; Cheng, L. X.; Shen, X. Y., Pollution levels and
138 characteristics of phthalate esters in indoor air of offices. *Journal of Environmental*
139 *Sciences-China* **2015**, *28*, 157-162.
- 140 (3) Pei, X. Q.; Song, M.; Guo, M.; Mo, F. F.; Shen, X. Y., Concentration and risk assessment of
141 phthalates present in indoor air from newly decorated apartments. *Atmos. Environ.* **2013**, *68*,
142 17-23.
- 143 (4) Bergh, C.; Torgrip, R.; Emenius, G.; Ostman, C., Organophosphate and phthalate esters in air and
144 settled dust - a multi-location indoor study. *Indoor Air* **2011**, *21*, (1), 67-76.
- 145 (5) Rudel, R. A.; Dodson, R. E.; Perovich, L. J.; Morello-Frosch, R.; Camann, D. E.; Zuniga, M. M.;
146 Yau, A. Y.; Just, A. C.; Brody, J. G., Semivolatile Endocrine-Disrupting Compounds in Paired
147 Indoor and Outdoor Air in Two Northern California Communities. *Environ. Sci. Technol.* **2010**, *44*,
148 (17), 6583-6590.
- 149 (6) Kanazawa, A.; Saito, I.; Araki, A.; Takeda, M.; Ma, M.; Saijo, Y.; Kishi, R., Association between
150 indoor exposure to semi-volatile organic compounds and building-related symptoms among the
151 occupants of residential dwellings. *Indoor Air* **2010**, *20*, (1), 72-84.
- 152 (7) Fromme, H.; Lahrz, T.; Piloty, M.; Gebhart, H.; Oddoy, A.; Ruden, H., Occurrence of phthalates and
153 musk fragrances in indoor air and dust from apartments and kindergartens in Berlin (Germany).
154 *Indoor Air* **2004**, *14*, (3), 188-195.
- 155 (8) Rudel, R. A.; Camann, D. E.; Spengler, J. D.; Korn, L. R.; Brody, J. G., Phthalates, alkylphenols,
156 pesticides, polybrominated diphenyl ethers, and other endocrine-disrupting compounds in indoor
157 air and dust. *Environ. Sci. Technol.* **2003**, *37*, (20), 4543-4553.
- 158 (9) Johnson-Restrepo, B.; Kannan, K., An assessment of sources and pathways of human exposure to
159 polybrominated diphenyl ethers in the United States. *Chemosphere* **2009**, *76*, (4), 542-548.
- 160 (10) USEPA. Exposure Factors Handbook: 2011 Edition. Washington, DC, United States
161 Environmental Protection Agency, Office of Research and Development C. 2011. Available from:
162 <http://www.epa.gov/ncea/efh/pdfs/efh-complete.pdf>.
- 163 (11) Chinese National Physique Monitoring Communique 2010 (in Chinese). Available from:
164 http://www.gov.cn/test/2012-04/19/content_2117320.htm.
- 165 (12) USEPA. Risk Assessment Guidance for Superfund, Human Health Evaluation Manual, Pt E,
166 Supplemental Guidance for Dermal Risk Assessment. vol. 1, USEPA, EPA 540-R-99-005,
167 Washington, DC. Available through: Springfield, VA, National Technical Information Service,
168 PB99-963312. 2004. Available from: <http://www.epa.gov/oswer/riskassessment/ragse/index.htm>.
- 169 (13) Guo, Y.; Kannan, K., Comparative Assessment of Human Exposure to Phthalate Esters from
170 House Dust in China and the United States. *Environ. Sci. Technol.* **2011**, *45*, (8), 3788-3794.
- 171