Supporting Information

Measurements of Parameters Controlling the Emissions of Organophosphate Flame Retardants in Indoor Environments

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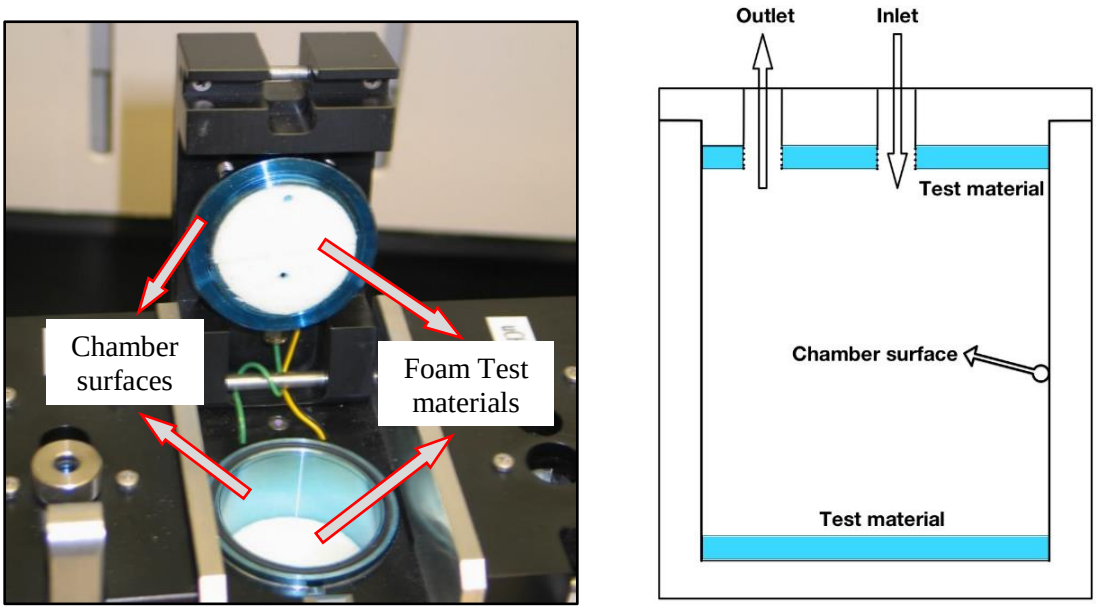
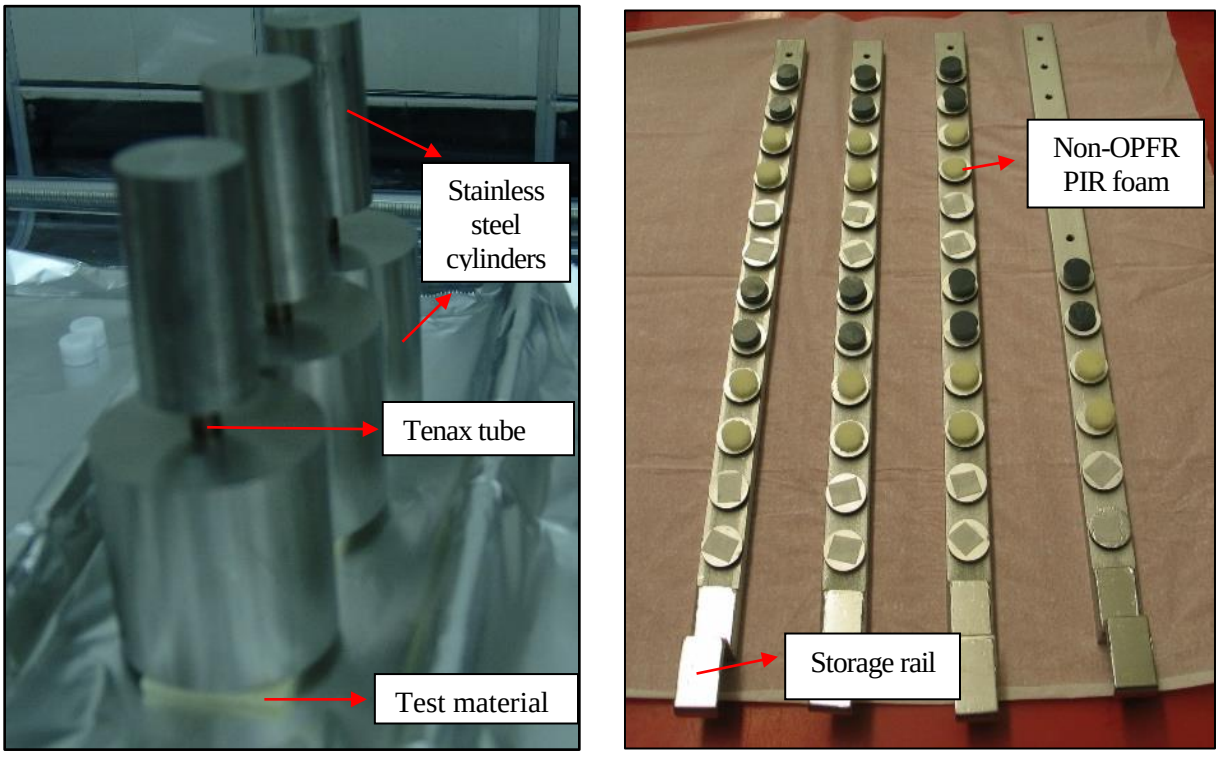


a) b)

Figure S1**. a)** A microchamber with source materials and b) Schematic diagram of the M-A-M microchamber.



a) b)

Figure S2**.** a) Diffusive tube sampling test (from bottom to top: position 1, position 2, and position 3) and b) Materials for small chamber sorption test on storage rail.

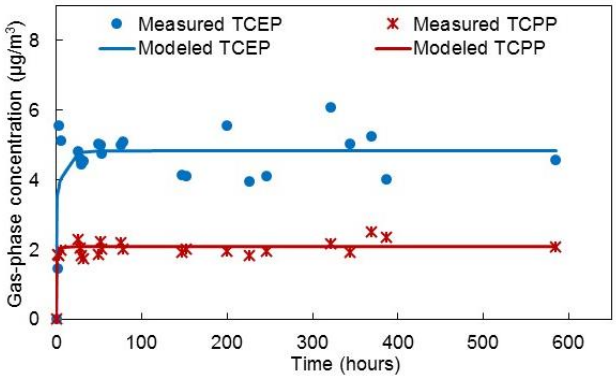
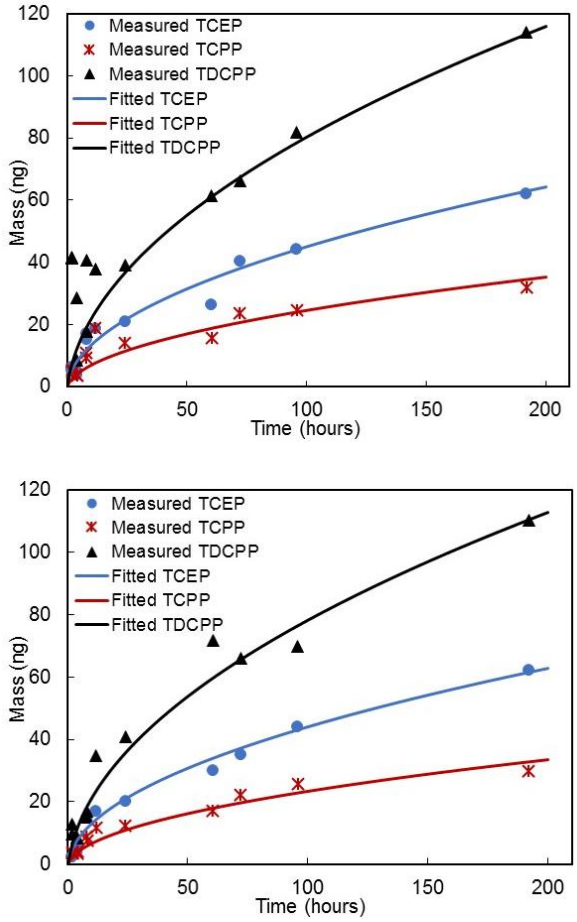


Figure S3. Measured gas-phase OPFR concentrations in the M-A-M microchamber with model fitting in chamber 2.



a) b)

Figure S4. The mass accumulation of TCEP, TCPP and TDCPP from diffusive sampling test with model fitting. a) Position 2, b) Position 3.

Table S1. Methods of Markes TD100 Agilent 6890/5973 GC/MS for OPFRs analysis

Operating Mode		Standard Two Stage	
	Flow Path Temp	180	°C
	Min Carrier Pressure	8.0	psi
	GC Cycle Time	19.0	min
Standby Mode			
	Split	On	
	Split Flow	20.0	mL/min
Pre-desorption		Purge Settings	
	Inject Std	1.0	min
	IS Flow	40.0	mL/min
	Loop Fill Time	1.0	min
	Prepurge Time	0.1	min
	Split On	20.0	mL/min
Tube/Sample Desorption			
	Desorption Time	8.0	min
	Desorption Temp	300	°C
	Trap Flow	50.0	mL/min
	Split	On	
	Inlet Split Ratio	2.4:1	
Trap Settings		Trap Desorption Settings	
	Pre Trap Fire Purge	1.0	min
	Trap Flow	35.0	mL/min
	Split Flow	34.0	mL/min
	Outlet Split Ratio	35.0:1	
	Total Split Ratio	85.0:1	
	Trap Low Temp	25	°C
	Heating Rate	MAX	°C/min
	Trap High Temp	310	°C
	Trap Hold Time	3.0	min

Table S2. Methods of Agilent 6890/5973 GC/MS for tris organophosphorus flame retardants.

Parameters	Settings
Method run time	12.5 minutes
Column model	Restek Rxi-5 Sil MS
Column dimensions	30 m x 0.25 mm 0.25 µm
Carrier gas	Helium
Flow rate	1.0 mL/min
Oven temperature gradient	80 °C hold for 0.5 min; 20 °C/min to 300 °C for 1 min; post run 325 °C for 8 min
Injector type	Agilent split/splitless
Inlet mode	Pulsed Splitless
MSD interface	280 °C
Source temperature	230 °C
MS Quad temperature	180 °C
Acquisition mode	SIM
Solvent delay	6.50 min
Inlet temperature	250 °C; pulsed pressure 30 psi for 2.1 min; purge time 2 min; purge flow 35 mL/min.
SIM Parameters	6.50 – 7.59 min, 103 m/z (TBP-L)[1]; 7.60 – 9.49 min, 249 m/z (TCEP)[2], 277 m/z (TCPP)[3]; 9.5 –12.5 min, 381 m/z (TDCPP)[4], 341 m/z (TPP-L)[5]

1. d_{27} - tributyl phosphate, internal standard.
2. tris(2-chloroethyl) phosphate.
3. tris(1-chloro-2-propyl) phosphate.
4. tris(1,3-dichloro-2-propyl) phosphate.
5. d_{15}-triphenyl phosphate, recovery check standard.

Table S3. Quantification ranges of OPFRs for the tests in this study.

Tests	Unit	TCEP	TCPP	TDCPP
Micro chamber emission test	ng/mL	5 - 202	5 - 204	5 - 202
Diffusive sampling test	ng	10 - 250	10 - 600	10 - 200
Dual small chamber sorption test	ng/mL	5 - 202	5 - 204	5 - 202

Table S4. Parameters used for model fitting for the M-A-M microchamber emission test, the diffusive sampling test, and the dual small chamber sorption test.

Tests	Parameters at 23°C		TCEP	TCPP	TDCPP
Microchamber emission test	Chamber volume (V) [1]	m^3		4.4×10^{-5}	
	Ventilation rate (Q) [1]	m^3/h		1.2×10^{-2}	
	Air change rate (ACH) [1]	h^{-1}		273	
	Average air velocity in chamber [2]	m/s		0.09	
	Emission surface area (A_0) [1]	m^2		3.2×10^{-3}	
	Chamber surface area (A_s) [1]	m^2		3.5×10^{-3}	
	Material-phase concentration in foam (C_0) [1]	$\mu g/m^3$	9.04×10^{8}	5.33×10^{8}	3.09×10^{9}
	Steady state gas-phase concentration in chamber 1 (y_{ss}±%RSD) [1]	$\mu g/m^3$	5.02 ±10.66	2.02 ±13.64	N/A
	Steady state gas-phase concentration in chamber 2 (y_{ss}±%RSD) [1]	$\mu g/m^3$	4.65 ±10.4	2.07 ± 10.46	N/A
	Mass transfer coefficient (h_m, h_s) [3]	m/h	4.92	4.55	4.28
	Chamber surface/air partition coefficient (K_{sa}) [4]	m	29.40	6.20	N/A
	Tenax tube internal diameter [1]	m		0.005	
Diffusive sampling test	Thickness of washer [1]	m		1.40×10^{-4}	
	Diffusive length [5]	m		0.014	
	Diffusivity in air [6]	m^2/s	5.37×10^{-6}	4.77×10^{-6}	4.35×10^{-6}
	Chamber volume (V) [1]	m^3		0.053	
	Ventilation rate (Q) [1]	m^3/h		5.56×10^{-2}	
	Air change rate (ACH) [1]	h^{-1}		1.05	
Dual small chamber sorption test	Average air velocity in chamber [2]	m/s		0.17	
	Material surface area [1]	m^2		5.62×10^{-4}	
	Thickness of material [1]	m		3.97×10^{-3}	
	Inlet gas-phase concentration [1]	$\mu g/m^3$	1.11	5.00	0.16
	Molecular weight	g/mol	285.5	327.6	430.9
	Vapor pressure [7]	torr	8.55×10^{-6}	1.05×10^{-5}	4.20×10^{-8}

1. Measured in the test.
2. Air velocity measured following the method in ref 1.
3. Calculated with the measured air velocity in microchamber using program PARAMS.[2] h_m and h_s in Equation 3 have the same value because of the same measured air velocity in microchamber.
4. Obtained from ref 1.
5. Obtained from ref 3.
6. Estimated using program PARAMS.[2]
7. Obtained from ref 4.

Table S5. Calculated Bi_m/K_{ma} and Fo_m values of SVOCs for different materials.

Material	Chemical	D_m (m^2/h)	K_{ma}	h_m (m/h)[5]	L (mm)	Bi_m/K_{ma}	Fo_m[6]
PIR foam[1]	TCEP	2.01E-10	7.76E+06	1.35	3.97	3.43	7.67E-03
	TCPP	8.25E-11	6.85E+06	1.25	3.97	8.78	3.14E-03
	TDCPP	1.39E-11	1.90E+08	1.18	3.97	1.77	5.28E-04
Plastic sheet[1]	TCEP	4.98E-11	2.00E+07	1.35	0.1	0.14	2.99E+00
	TCPP	2.04E-11	1.91E+07	1.25	0.1	0.32	1.22E+00
	TDCPP	3.43E-12	6.31E+07	1.18	0.1	0.54	2.06E-01
Vinyl flooring[1]	TCEP	8.81E-12	4.74E+08	1.35	4.62	1.50	2.48E-04
	TCPP	3.61E-12	4.34E+08	1.25	4.62	3.69	1.01E-04
	TDCPP	6.07E-13	4.62E+09	1.18	4.62	1.93	1.71E-05
Painted gypsum board[2]	TCEP	5.83E-09	3.85E+06	1.35	1.6	0.10	1.37E+00
	TCPP	2.39E-09	3.74E+06	1.25	1.6	0.22	5.60E-01
	TDCPP	4.02E-10	8.03E+06	1.18	1.6	0.58	9.42E-02
Concrete[2]	TCEP	9.03E-10	5.67E+06	1.35	6.3	1.66	1.37E-02
	TCPP	3.70E-10	5.39E+06	1.25	6.3	3.95	5.59E-03
	TDCPP	6.22E-11	2.11E+07	1.18	6.3	5.64	9.40E-04
Ceiling tile[2]	TCEP	2.94E-11	4.77E+07	1.35	1.1	1.06	1.46E-02
	TCPP	1.20E-11	4.10E+07	1.25	1.1	2.79	5.95E-03
	TDCPP	2.02E-12	3.99E+08	1.18	1.1	1.60	1.00E-03
Vinyl flooring-A[2]	TCEP	1.15E-11	2.09E+07	1.35	0.2	1.13	1.73E-01
	TCPP	4.73E-12	1.89E+07	1.25	0.2	2.80	7.10E-02
	TDCPP	7.95E-13	2.53E+08	1.18	0.2	1.17	1.19E-02
Mattress pad liner[2]	TCEP	5.73E-12	2.08E+07	1.35	0.2	2.27	8.60E-02
	TCPP	2.35E-12	1.96E+07	1.25	0.2	5.43	3.53E-02
	TDCPP	3.94E-13	9.72E+07	1.18	0.2	6.14	5.91E-03
Polyester clothing[2]	TCEP	1.64E-13	3.35E+06	1.35	2.2	5414	2.03E-05
	TCPP	6.70E-14	2.89E+06	1.25	2.2	14202	8.31E-06
	TDCPP	1.13E-14	1.54E+08	1.18	2.2	1485	1.40E-06
Cotton clothing[2]	TCEP	1.52E-11	1.03E+07	1.35	0.8	6.91	1.43E-02
	TCPP	6.24E-12	9.67E+06	1.25	0.8	16.57	5.85E-03
	TDCPP	1.05E-12	4.82E+07	1.18	0.8	18.57	9.84E-04
Uniform shirt[2]	TCEP	1.45E-10	2.58E+06	1.35	0.8	2.89	1.36E-01
	TCPP	5.92E-11	2.39E+06	1.25	0.8	7.07	5.55E-02
	TDCPP	9.96E-12	1.84E+07	1.18	0.8	5.13	9.34E-03
PUF[2]	TCEP	1.22E-09	5.28E+06	1.35	7.1	1.49	1.45E-02
	TCPP	5.01E-10	4.99E+06	1.25	7.1	3.55	5.96E-03
	TDCPP	8.43E-11	2.26E+07	1.18	7.1	4.38	1.00E-03

Painted Gypsum board[2]	TCEP	2.66E-09	5.01E+06	1.35	1.1	0.11	1.32E+00
	TCPP	1.09E-09	4.85E+06	1.25	1.1	0.26	5.40E-01
	TDCPP	1.83E-10	1.17E+07	1.18	1.1	0.60	9.07E-02
PUF[2]	TCEP	2.95E-09	3.87E+06	1.35	8.9	1.05	2.23E-02
	TCPP	1.21E-09	3.70E+06	1.25	8.9	2.48	9.17E-03
	TDCPP	2.03E-10	1.23E+07	1.18	8.9	4.19	1.54E-03
Carpet-B[2]	TCEP	9.60E-09	5.70E+05	1.35	5.8	1.43	1.71E-01
	TCPP	3.93E-09	5.30E+05	1.25	5.8	3.48	7.01E-02
	TDCPP	6.61E-10	3.74E+06	1.18	5.8	2.76	1.18E-02
Vinyl flooring-B[2]	TCEP	2.23E-12	9.42E+07	1.35	0.2	1.29	3.35E-02
	TCPP	9.13E-13	9.20E+07	1.25	0.2	2.98	1.37E-02
	TDCPP	1.54E-13	1.74E+08	1.18	0.2	8.77	2.31E-03
Mattress pad[2]	TCEP	4.70E-10	3.14E+05	1.35	0.8	7.33	4.41E-01
	TCPP	1.92E-10	2.72E+05	1.25	0.8	19.15	1.80E-01
	TDCPP	3.23E-11	1.38E+07	1.18	0.8	2.11	3.03E-02
PTFE[3]	PCB-52	1.17E-15	6.18E+06	1.31	0.8	112388	1.10E-06
	PCB-66	1.17E-15	2.35E+07	1.31	0.8	144386	1.10E-06
	PCB-101	5.65E-16	3.60E+07	1.22	0.8	37971	5.30E-07
	PCB-110	5.65E-16	6.76E+07	1.22	0.8	47906	5.30E-07
	PCB-118	5.65E-16	1.44E+08	1.22	0.8	25512	5.30E-07
PEEK[3]	PCB-52	1.78E-16	2.93E+07	1.31	2.4	11976	1.85E-08
	PCB-66	1.78E-16	1.07E+08	1.31	2.4	600529	1.85E-08
	PCB-101	8.61E-17	1.61E+08	1.22	2.4	164444	8.97E-09
	PCB-110	8.61E-17	2.97E+08	1.22	2.4	210877	8.97E-09
	PCB-118	8.61E-17	6.16E+08	1.22	2.4	114314	8.97E-09
Polypropylene sheet[3]	PCB-52	1.33E-10	9.14E+06	1.31	0.8	0.86	1.25E-01
	PCB-66	1.33E-10	2.49E+07	1.31	0.8	0.32	1.25E-01
	PCB-101	6.46E-11	3.44E+07	1.22	0.8	0.44	6.06E-02
	PCB-110	6.46E-11	5.52E+07	1.22	0.8	0.27	6.06E-02
	PCB-118	6.46E-11	9.73E+07	1.22	0.8	0.16	6.06E-02
HDPE Polyethylene sheet[3]	PCB-52	1.34E-10	1.28E+07	1.31	0.8	0.61	1.26E-01
	PCB-66	1.34E-10	3.13E+07	1.31	0.8	0.25	1.26E-01
	PCB-101	6.47E-11	4.16E+07	1.22	0.8	0.36	6.07E-02
	PCB-110	6.47E-11	6.34E+07	1.22	0.8	0.24	6.07E-02
	PCB-118	6.47E-11	1.05E+08	1.22	0.8	0.14	6.07E-02
LDPE Polyethylene sheet [3]	PCB-52	3.18E-10	1.66E+07	1.31	0.8	0.20	2.98E-01
	PCB-66	3.18E-10	2.98E+07	1.31	0.8	0.11	2.98E-01
	PCB-101	1.54E-10	3.60E+07	1.22	0.8	0.18	1.44E-01
	PCB-110	1.54E-10	4.75E+07	1.22	0.8	0.13	1.44E-01
	PCB-118	1.54E-10	6.62E+07	1.22	0.8	0.10	1.44E-01

Concrete disks[3]	PCB-52	1.26E-11	1.29E+07	1.31	7.2	57.81	1.46E-04
	PCB-66	1.26E-11	3.47E+07	1.31	7.2	21.49	1.46E-04
	PCB-101	6.12E-12	4.76E+07	1.22	7.2	30.10	7.08E-05
	PCB-110	6.12E-12	7.60E+07	1.22	7.2	18.85	7.08E-05
	PCB-118	6.12E-12	1.33E+08	1.22	7.2	10.77	7.08E-05
Vinyl flooring[4]	DEHP	3.60E-10	2.40E+11	1.05	2.0	2.44E-05	5.40E-02

1. Measured in this study.
2. The values of D_m, K_{ma}, L were obtained from ref 5.
3. The values of D_m, K_{ma}, L were obtained from ref 6.
4. The values of D_m, K_{ma}, L were obtained from ref 7.
5. Calculated using program PARAMS (ref 2) with an air velocity of 0.85 m/s (ref 8) and a characteristic length of 1 m (reasonably assumed).
6. Estimated with a time of 600 h (emission test duration in this study).

Table S6. Relationship between y_0/V_p and mass fraction in materials for SVOCs.

	Mass fraction	y_0 (μg/m^3)	V_p at 25 °C (μg/m^3)[1]	y_0/V_p
DEHP[1]	0.13	2.3	5.64	0.41
DEHP[1]	0.001	0.02	5.64	0.004
DEHP[1]	0.07	1.54	5.64	0.27
DEHP[2]	0.05	0.77	5.64	0.14
DEHP[3]	0.06	0.9	5.64	0.16
DINP[1]	0.20	0.42	0.52	0.81
BBP[1]	0.15	8.47	12.3	0.69
Iso-DEHP[1]	0.07	0.12	0.88	0.14
DnBP[1]	0.09	24.7	464	0.053
DnBP[2]	0.04	36	464	0.078
DnBP[3]	0.04	25	464	0.054
TCEP[4]	0.04	5.79	131[6]	0.044
TCEP[5]	0.04	4.33	131 [6]	0.033
TCPP[4]	0.02	2.45	185 [6]	0.013
TCPP[5]	0.02	1.67	185 [6]	0.009

1. Obtained from ref 9.
2. Obtained from ref 10.
3. Obtained from ref 3.
4. Obtained from the material-air-material (M-A-M) configured microchamber emission test in this study.
5. Obtained from the diffusive sampler test in this study.
6. Obtained from ref 4. The vapor pressure values were converted from Pa to μg/m^3 using the ideal gas law.

REFERENCES

1. Liang, Y.; Liu, X.; Allen, M. R. Measuring and modeling surface sorption dynamics of organophosphate flame retardants in chambers. *Chemosphere* **2018**, 193, 754-762.
2. Guo, Z. Program PARAMS Users Guide. U.S. Environmental Protection Agency, Washington, DC, EPA/600/R-05/066 (NTIS PB2006-102000), **2005.**
3. Wu, Y.; Xie, M.; Cox, S. S.; Marr, L. C.; Little, J. C., A simple method to measure the gas-phase SVOC concentration adjacent to a material surface. *Indoor Air* **2016**, 26, 903-912.
4. European Union Risk Assessment Report - TDCP CAS 13674-87-8, May 2008. Tris [2-Chloro-1-(Chloromethyl) Ethyl] Phosphate (TDCP). https://echa.europa.eu/documents/10162/13630/trd_rar_ireland_tdcp_en.pdf (last accessed April 17, **2018**).
5. Liu, X.; Allen, M. R.; Roache, N. F., Characterization of organophosphorus flame retardants' sorption on building materials and consumer products. *Atmos. Environ*. **2016**, 140, 333-341.
6. Liu, X.; Guo, Z.; Roache, N. F., Experimental method development for estimating solid-phase diffusion coefficients and material/air partition coefficients of SVOCs. *Atmos. Environ*. **2014**, 89, 76-84.
7. Xu, Y.; Little, J. C., Predicting emissions of SVOCs from polymeric materials and their interaction with airborne particles. *Environ. Sci. Technol.* **2006**, 40, 456-461.
8. Huang, J. M.; Chen, Q. Y.; Ribot, B.; Rivoalen, H., Modelling contaminant exposure in a single-family house. *Indoor Built Environ.* **2004**, 13, 5-19.
9. Liang, Y.; Xu, Y., Improved method for measuring and characterizing phthalate emissions from building materials and its application to exposure assessment. *Enviro. Sci. Technol*. **2014**, 48, 4475-4484.
10. Cao, J.; Zhang, X.; Little, J. C.; Zhang, Y., A SPME-based method for rapidly and accurately measuring the characteristic parameter for DEHP emitted from PVC floorings. *Indoor Air* **2017**, 27, 417-426.