

Supplemental Materials for:

Assessment of spray polyurethane foam workers exposure to organophosphate flame retardants through measures in air, hand wipes and urine

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Supplemental Experimental Method

The analysis of air sampling media and surface wipe extracts for organophosphate flame retardants (OPFRs): tris(1-chloro-2-propyl) phosphate (TCPP) and tris(1,3-dichloro-2-propyl) phosphate (TDCPP), were completed by the ultra-performance liquid chromatography (UPLC) - atmospheric pressure photoionization (APPI) tandem mass spectrometry method modified from La Guardia et al. (2015). Briefly, media were subjected to accelerated solvent extraction (ASE 200, Dionex, Sunnyvale, CA, USA) with dichloromethane (DCM). Surrogate standards (6000 ng of deuterated tris (1,3-dichloro-2-propyl) phosphate (*d*TDCPP); MPI for Biophysical Chemistry, Goettingen, Germany, 630 ng of deuterated triphenyl phosphate (*d*15-TPP); Sigma-Aldrich, Corp., St. Louis, MO., USA) are added to each sample prior to extraction. For hand wipe only: extracts are purified by size exclusion chromatography (SEC, Envirosep-ABC®, 350 x 21.1 mm. column; Phenomenex, Torrance, CA, USA). Eluent DCM, at 5 mL min.⁻¹. For all media: each post-SEC extract is solvent exchanged to hexane, reduced in volume and added to the top of a solid phase 2-g silica glass extraction column (Isolute, International Sorbent Tech.; Hengoed Mid Glamorgan, UK). Each column is eluted with 3.5-mL hexane (fraction one), followed by 6.5 mL of 60:40 hexane/DCM and 8 mL DCM (fraction two) and 5 ml 50:50 acetone/DCM (fraction three). Fraction three containing OPFRs are reduced, solvent exchanged to methanol and 800 ng of decachlorodiphenyl ether (DCDE) (AccuStandard, New Haven, CT., USA) is added as an internal standard. Analytes in the purified extract are chromatographically separated by UPLC (Acquity UPLC, Waters Corporation, Milford, MA., USA) operated in the gradient mode (100%

methanol (A1) and 100% water (B1)), equipped with a C18 UPLC analytical column (Acquity UPLC BEH C18, 1.7 μ m, 2.1x150 mm, Waters Corp.). Analytes are ionized by APPI, the dopant (acetone) is introduced (150 μ l min⁻¹) by a liquid chromatography pump (LC-20AD, Shimadzu Corporation, Kyoto, Japan) and product ions are detected by triple quadrupole mass spectrometer (3200 QTrap, AB Sciex, Framingham, MA., USA) operated in the Multiple Reaction Monitoring (MRM) mode for TCPP and *d*TDCPP (quantitation ions m/z 35 ([³⁵Cl]⁻), 37([³⁷Cl]⁻)).

References

La Guardia, M. J., Hale, R. C., [2015]. Halogenated flame-retardant concentrations in settled dust, respirable and inhalable particulates and polyurethane foam at gymnastic training facilities and residences. *Environ. Int.* 79, 106 – 114.

Table S1. TCPP and TDCPP percent by weight in bulk samples^A

State Company Located	Brand	Year sample collected	Product	Open or Closed	Cured TDCPP %	Cured TCPP %	Side B TCPP %
PA	Lapolla	2017	Foam-Lok 400 (Houston, TX)	Open	0.0202	3.20	35.42
PA	Lapolla	2017	Foam-Lok CCRR- 1025 (Houston, TX)	Closed	0.0124	1.24	7.85
PA	Demilec	2017	Heatlok XT (Arlington, TX)	Closed	^B	^B	1.94
RI	Icynene	2015	LD-C-50™ (Mississauga, Ontario, Canada)	Open	ND	12.05	18.35
RI	Icynene	2015	MD-C-200™ (Mississauga, Ontario, Canada)	Closed	ND	3.14; 1.95 ^C	6.84
TN	Bayer/CertainTeed	2015	BaySeal CCX ISO (Pittsburgh, PA) /Certaspray X (Valley Forge, PA)	Open	ND	13.31	20.63
TN	Bayer	2015	Bayseal OC (Pittsburgh, PA)	Open	ND	8.69	20.63
TN	Bayer	2015	Bayseal CCX (Pittsburgh, PA)	Closed	ND	2.96	3.99
TN	CertainTeed	2015	Certaspray X (Valley Forge, PA)	Open	0.0961	12.67	^D
TN	Unknown ^E	2015	Unknown	Open	ND	12.5 ^{C,D}	^B
KS	Demilec	2015	Heatlok Soy 200 (Arlington, TX)	Closed	ND	5.51	4.24
KS	Demilec	2015--	Sealection 500 (Arlington, TX)	Open	ND	17.36	16.78
NY	Demilec	2017	Heatlok Highlift (Arlington, TX)	Closed	ND	0.99	7.06
NY	NCFI Polyurethane	2017	InsulBloc R-11-017- GL (Mount Airy, NC)	Closed	ND	0.42	2.86
OH	PSI (Preferred Solutions Inc)	2015	Staycell One Step 255 (Cleveland, OH)	Closed	ND	1.22	6.28

A. LOD was 0.10 – 100 µg/g for TCPP and TDCPP.

B. Sample was not collected at this site.

C. Two samples of cured foam were taken.

D. An error occurred within the contract lab during analysis.

E. Workers identified the cured foam as open-cell that had been sprayed on a previous day, but we were not able to determine the brand and type.

Table S2. Summary of TCPP percent by weight in bulk samples^A

Type^B	Cured^C			Side B		
	N	Median (%)	GM (GSD) (%)	N	Median (%)	GM (GSD) (%)
Closed	8	1.59	1.68 (2.13)	8	5.26	4.66 (1.59)
Open	7	12.46 ^B	9.23 (1.66)	4	19.49	17.73 (1.33)

A. LOD was 0.10 – 100 µg/g for TCPP and TDCPP.

B. Open vs closed: p value < 0.001 for paired t-test.

C. Includes two cured samples where the brand was unknown

Table S3. TCPP TWA air sampling concentrations^A using paired t-test and one-way analysis of variance ($\mu\text{g}/\text{m}^3$)

	N	Median	GM (GSD)	25th - 75th percentiles	Range	P-value
Overall	29	39.6	48.5 (3.63)	25.5 – 120	2.62 – 519	
Job Position						0.025 ^D
Sprayer	13	98.7	87.1 (3.10)	37.5 – 162	15.5 – 519	
Helper	16	30.8	30.2 (3.47)	18.8 – 79.5	2.62 - 196	
Respirators Worn During Spraying^B						0.969 ^E
None						
Sprayer	1	37.1	C	C	C	
Helper	7	39.6	42.3 (4.28)	25.5 – 145	2.62 – 196	
Half-face air-purifying						
Sprayer	4	135	132 (3.09)	59.6 – 354	37.5 – 519	
Helper	6	25.6	24.5 (2.60)	14.7 – 28.8	6.58 – 120	
Full-face air-purifying						
Sprayer	2	88.8	50.2 (5.25)	C	15.5 – 162	
Helper	1	39.6	C	C	C	
Supplied air						
Sprayer	6	108	91.6 (3.20)	41.8 – 157	16.1 – 483	
Helper	2	31.6	14.9 (7.05)	3.75 – 59.4	3.75 – 59.4	

- A. All samples were above LOD. LOD for TCPP was 1, 8, or 15.6 ng/sample for OVS samples
 B. Air was sampled outside of the respirator.
 C. Not enough samples to calculate central tendencies.
 D. Paired t-test was utilized for comparisons.
 E. One-way analysis of variance (ANOVA) was utilized for comparisons for respirator (none, half-face air-purifying, full-face air-purifying, and supplied air).

Table S4. TDCPP hand wipe sampling concentrations^{A,B,C} (ng/wipe)

Job Position	Sample Collection	N	Median	GM (GSD)	25th - 75th percentiles	Range
Sprayer	Pre	9	157	112 (4.79)	62.5 – 233	<LOD – 828
Sprayer	Post	9	261	240 (2.28)	187 – 329	67.4 – 830
Helper	Pre	6	292	325 (3.10)	122 – 731	92.2 – 1840
Helper	Post	6	278	324 (2.37)	168 – 749	115 – 1,060
Total		30	234	215 (3.29)	128 – 360	<LOD – 1,840
Gloves^D						
No		2	E	E	E	321 – 749
Yes		8	177	180 (2.23)	95.8 – 266	67.4 – 830
Intermittent		5	E	E	E	235 – 1,060
Hand washing^D						
Yes		8	321	267 (2.26)	168 – 585	67.4 – 749
No		7	250	273 (2.42)	175 – 551	76.5 – 1,060

A. TDCPP was measured at four of six companies.

B. LOD is 5 or 10 ng/sample for dermal samples

C. Differences were not significant between sprayer pre- and post-shift, helper pre- and post-shift, gloves or hand washing.

D. Results include only post samples

E. Not enough samples to calculate central tendencies.

Table S5. Urine sampling concentrations^A using paired t-test and student's t-test (µg/g cr)

Analyte ^B	Sample Collection	N	No. <LOD ^A (%)	Median	GM (GSD)	25 th - 75 th %tiles	Range	P-value
BCPP								
	Pre	29	0 (0)	13.7	16.2 (4.45)	4.82 – 40.7	1.79 – 830	< 0.001 ^E
	Post	29	0 (0)	37.2	35.0 (3.82)	19.8 – 57.6	1.78 – 1,620	
	Total	58	0 (0)	29.9	23.8 (4.30)	8.99 – 52.1	1.78 – 1,620	
BCPP General Population^C	Total	924	376 (40.7)	0.15	0.16 (2.71)	0.08 – 0.28	0.01 – 27.0	< 0.001 ^F
BDCPP								
	Pre	29	0 (0)	2.59	2.60 (2.33)	1.84 – 3.81	0.23 – 25.7	0.491 ^E
	Post	29	0 (0)	2.42	2.79 (2.26)	1.79 – 4.92	0.32 – 16.8	
	Total	58	0 (0)	2.53	2.69 (2.28)	1.79 – 4.36	0.23 – 25.7	
BDCPP General Population^C	Total	911	69 (7.6)	0.65	0.66 (2.77)	0.32 – 1.30	0.05 – 67.9	< 0.001 ^F
BCEtP								
	Pre	29	3 (10)	0.36	0.44 (2.77)	0.26 – 0.98	0.04 – 2.17	0.435 ^E
	Post	29	2 (6.9)	0.43	0.46 (3.14)	0.26 – 1.01	0.03 – 21.2	
	Total	58	5 (8.6)	0.41	0.45 (2.93)	0.26 – 1.01	0.03 – 21.2	
BCEtP General Population^C	Total	920	105 (11.4)	0.32	0.38 (3.23)	0.17 – 0.73	0.02 – 147	0.711 ^F
DBuP								
	Pre	29	4 (14)	0.11	0.14 (4.28)	0.04 – 0.19	0.04 – 0.42	0.131 ^E
	Post	29	4 (14)	0.14	0.24 (6.16)	0.08 – 0.51	0.01 – 22.0	
	Total	58	9 (14)	0.13	0.18 (5.15)	0.04 – 0.08	0.01 – 22.0	
DBUP General Population^C	Total	922	184 (20)	0.18	0.16 (2.38)	0.10 – 0.27	0.01 – 9.00	0.059 ^F
DPhP								
	Pre	29	1 (3.4)	0.68	0.74 (2.66)	0.40 – 1.04	0.17 – 19.9	0.500 ^E
	Post	29	1 (3.4)	0.86	0.94 (1.88)	0.69 – 1.31	0.245 – 4.66	
	Total	58	2 (3.4)	0.76	0.83 (2.28)	0.55 – 1.16	0.169 – 19.9	
								0.166 ^F

Table S5. Urine sampling concentrations^A using paired t-test and student's t-test (µg/g cr), continued

Analyte ^B	Sample Collection	N	No. <LOD ^A (%)	Median	GM (GSD)	25 th - 75 th %tiles	Range	P-value
DPhP General Population^C	Total	921	85 (9.2)	0.55	0.58 (2.25)	0.34 – 0.94	0.04 – 29.6	
DpCP	Pre	29	20 (69)	D	D	D	0.01 – 0.18	D
	Post	29	23 (79)	D	D	D	0.01 – 0.19	
	Total	58	43 (74)	D	D	D	0.01 – 0.19	
DpCP General Population^C	Total	924	815 (88)	D	D	0.02 – 0.06	0.01 – 5.14	D
TBBA	Pre	29	22 (76)	D	D	D	0.01 – 0.97	D
	Post	29	18 (62)	D	D	D	0.01 – 0.69	
	Total	58	40 (69)	D	D	D	0.01 – 0.97	
TBBA General Population^B	Total	924	882 (95)	D	D	0.02 – 0.05	0.01 – 5.14	D

A. Limit of detection (LOD) for each analyte in µg/L: BCPP =0.10, BDCPP =0.11, BCEtP=0.08, DBuP =0.05, DPHP =0.16, DpCP =0.05, TBBA=0.05.

B. Not listed in table due to all samples being below LOD: DBzB=0.05, DoCP=0.05 µg/L.

C. Ospina, M; Jayatilaka, N; Wong, L; Restrepo, P., Calafat AM. Exposure to organophosphate flame retardant chemicals in the U.S. general population: Data from the 2013–2014 National Health and Nutrition Examination Survey. Environ. Int., 2018, 110,32-41 Includes male aged 18 +.

D. Not enough samples above LOD to calculate central tendencies.

E. Paired t-test was utilized for pre/post comparisons.

F. Student's t-test was utilized for SPF workers to the general population (male aged 18+).

Table S6. Urine sampling concentrations adjusted for specific gravity^A using paired t-test (µg/L)

Analyte ^B	Sample Collection	N	No. <LOD ^A (%)	Median	GM (GSD)	25 th - 75 th Percentiles	Range	P-value
BCPP								
	Pre	29	0 (0)	24.0	28.9 (4.49)	10.1 – 81.5	2.31 – 1,740	< 0.001
	Post	29	0 (0)	70.5	76.4 (4.05)	43.0 – 122	3.71 – 5,240	
	Total	58	0 (0)	52.9	47.0 (4.57)	13.4 – 104	2.31 – 5,240	
BDCPP								
	Pre	29	0 (0)	4.43	4.63 (2.55)	2.63 – 7.25	0.34 – 53.8	0.043
	Post	29	0 (0)	5.67	6.08 (2.52)	3.32 – 13.0	0.87 – 54.4	
	Total	58	0 (0)	4.74	5.30 (2.54)	3.05 – 8.78	0.34 – 54.4	
BCEtP								
	Pre	29	3 (10)	0.75	0.79 (3.01)	0.38 – 2.10	0.04 – 5.03	0.361
	Post	29	2 (6.9)	1.07	1.00 (3.19)	0.69 – 1.72	0.07 – 68.6	
	Total	58	5 (8.6)	1.03	0.89 (3.16)	0.41 – 1.81	0.04 – 68.6	
DBuP								
	Pre	29	4 (14)	0.169	0.24 (4.49)	0.10 – 0.32	0.04 – 10.3	0.126
	Post	29	4 (14)	0.313	0.52 (6.25)	0.16 – 1.40	0.03 – 48.6	
	Total	58	8 (14)	0.243	0.36 (5.50)	0.12 – 0.85	0.03 – 48.6	
DPhP								
	Pre	29	1 (3.4)	1.43	1.32 (2.37)	0.68 – 1.92	0.45 – 27.0	0.818
	Post	29	1 (3.4)	1.82	2.04 (2.07)	1.44 – 3.31	0.27 – 7.97	
	Total	58	2 (3.4)	1.62	1.65 (2.28)	0.95 – 2.65	0.27 – 27.0	
DpCP								
	Pre	29	20 (69)	C	C	C	0.03 – 0.29	C
	Post	29	23 (79)	C	C	C	0.03 – 0.32	
	Total	58	43 (74)	C	C	C	0.03 – 0.32	
TBBA								
	Pre	29	22 (72)	C	C	C	0.03 – 2.02	C
	Post	29	18 (60)	C	C	C	0.03 – 2.24	
	Total	58	40 (69)	C	C	C	0.03 – 2.24	

A. Limit of detection (LOD) for each analyte in µg/L: BCPP =0.10, BDCPP =0.11, BCEtP=0.08; DBuP =0.05; DPHP =0.16; DpCP =0.05, TBBA=0.05

B. Not listed in table due to all concentrations being below LOD: DBzB=0.05, DoCP=0.05 µg/L.

C. Not enough samples above LOD to calculate central tendencies.

Table S7. Urine sampling concentrations^A adjusted for specific gravity using paired t-test (µg/L)

Analyte	Sample Collection	Job Position	N	Median	GM (GSD)	25 th - 75 th %tiles	Range	P-value
BCPP^A								
	Pre	Sprayer	13	81.5	66.5 (4.37)	21.5 – 114	8.42 – 1,740	0.007
	Post	Sprayer	13	93.4	156 (3.94)	58.3 – 233	43.0 – 5,240	
	Pre	Helper	16	12.3	14.7 (3.24)	5.71 – 43.6	2.31 – 118	0.003
	Post	Helper	16	50.8	42.7 (3.19)	21.4 – 97.9	3.71 – 257	
BDCPP^A								
	Pre	Sprayer	13	4.50	4.71 (3.23)	3.05 – 7.25	0.34 – 53.8	0.085
	Post	Sprayer	13	5.67	6.55 (3.21)	2.94 – 17.6	0.87 – 54.4	
	Pre	Helper	16	4.10	4.56 (2.09)	2.59 – 7.41	1.27 – 18.0	0.247
	Post	Helper	16	6.05	5.73 (2.02)	3.53 – 9.21	1.74 – 15.5	

A. Limit of detection (LOD) for each analyte in µg/L: BDCPP =0.11, BCPP =0.10. All samples were above the LOD