

Supplemental Information

Supplemental Experimental Method (hand wipe and bulk foam)

The analysis of hand wipe and bulk foam extracts for brominated flame-retardants (BFRs): polybrominated diphenyl ethers (PBDEs: BDE-28, -47, -66, -85, -99, -100, -153), alternative-BFRs (alt-BFRs): 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (EH-TBB) and di (2-ethylhexyl)-2,3,4,5-tetrabromophthalate (BEH-TBPH)), chlorinated organophosphate flame retardants (ClOPFRs): tris (2-chloroethyl) phosphate (TCEP), tris (1-chloro-2-propyl) phosphate (TCIPP) and tris (1,3-dichloro-2-propyl) phosphate (TDCPP)) were completed by ultra-performance liquid chromatography (UPLC) - atmospheric pressure photoionization (APPI) tandem mass spectrometry as previously described by La Guardia et al. (2015). Briefly, wipes and bulk foam (~100 mg) were subjected to accelerated solvent extraction (ASE 200, Dionex, Sunnyvale, CA, USA) using dichloromethane (DCM). Surrogate standards (500 ng of 2,3,4,4', 5,6-hexabromodiphenyl ether (BDE-166) (Sigma-Aldrich, Corp., St. Louis, MO, USA) and 6000 ng of deuterated tris (1,3-dichloro-2-propyl) phosphate (dTDCPP); MPI for Biophysical Chemistry, Goettingen, Germany) were added to each sample prior to extraction. Extracts were 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. Each post-SEC extract was 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 was 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). Both fractions (fraction two containing BFRs and alt-BFRs and fraction three containing ClOPFRs) were reduced, solvent exchanged to methanol and 800 ng of decachlorodiphenyl ether (DCDE) (Sigma-Aldrich, Corp., St. Louis, MO, USA) was added as an internal standard. Analytes in these purified extracts were 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, 1.7µm, 2.1x150 mm, Waters Corp.). Analytes were ionized by APPI, the dopant (acetone) was introduced (150 µl/min.) by a liquid chromatography pump (LC-20AD, Shimadzu

Corporation, Kyoto, Japan) and product ions were detected by triple quadrupole mass spectrometer (3200 QTrap, AB Sciex, Framingham, MA, USA) operated in the Multiple Reaction Monitoring (MRM) mode. Quantitation ions for BFRs, alt-BFRs and BDE-166 are m/z 79 ([⁷⁹Br]⁻) and 81([⁸¹Br]⁻), and m/z 35 ([³⁵Cl]⁻), 37([³⁷Cl]⁻) for ClOPFRs, dTDCPP and DCDE. Analytes were quantified using a five point calibration curve (r² > 0.985), range; detection limit (dl) to 2,000 ng for BFRs and alt-BFRs and dl to 10,000 ng for ClOPFRs. Results for matrix spike recovery analysis are listed in NIOSH, 2016.

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.

NIOSH [2016]. Analytical method recovery of flame retardants from spiked gauze wipe media. Draft. Cincinnati, OH: U.S.

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Supplemental Table

Table S1. Replacement (new) and used (old) pit foam block flame retardant content (µg/g) by laboratory analysis

	New vs. old pit foam blocks											
	1	2	3	4	5	6	7	8	9	10	11	12
	New	New	New	New	Old	Old	Old	Old	Old	Old	Old	Old
BDE-28	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BDE-47	ND	ND	ND	ND	1.3	ND	8.7	14	6400	3.9	3.2	180
BDE-66	ND	ND	ND	ND	ND	ND	ND	ND	92	ND	ND	4.2
BDE-85	ND	ND	ND	ND	ND	ND	0.48	ND	520	ND	ND	11
BDE-100	ND	ND	ND	ND	ND	ND	2.8	1.8	1900	1.4	ND	49

BDE-99	ND	ND	ND	ND	ND	ND	13	10	11000	6.0	1.8	290
BDE-154	ND	ND	ND	ND	ND	ND	1.1	ND	850	ND	ND	20
BDE-153	ND	ND	ND	ND	ND	ND	1.2	ND	990	ND	ND	22
BDE-183	ND	ND	ND	ND	ND	ND	ND	ND	3.2	ND	ND	ND
BDE-206	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
BDE-209	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
EH-TBB	ND	24,000	27,000	7.5	27	190	13,000	29,000	1,300	9,500	21	19,000
BEH-TEBP	ND	5,200	6,300	4.5	7.4	41	5,800	12,000	320	4,300	8.0	6,500
BTBPE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
DBDPE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
α-HBCD	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
β-HBCD	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
γ-HBCD	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
TCEP	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
TCIPP	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
TDCPP	ND	2.2	ND	ND	35,000	21,000	2.5	ND	290	290	60,000	410
TBBPA	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

ND = not detected at or above 1 ng/sample.