GYMNAST EXPOSURE TO FLAME RETARDANTS

Carignan C[1], Heiger-Bernays W[1], McClean M[1], Sjödin A[2], Stapleton H[3], Webster TF[1]*

[1] Department of Environmental Health, Boston University School of Public Health, 715 Albany Street, Boston, MA, USA; [2] Centers for Disease Control and Prevention, National Center for Environmental Health, 4770 Buford Highway NE, Atlanta, GA 30341; [3] Nicholas School of the Environment, Duke University, A220 LSRC Box 90328, Durham, NC, USA

Introduction

PentaBDE is a chemical mixture of polybrominated diphenyl ethers (PBDEs) historically applied to polyurethane foam as a flame retardant, with most use in North America. Manufacture of PentaBDE in the U.S. was phased out starting in 2005. Restrictions on the use of PentaBDE have resulted in the increased use of alternative flame retardants such as tris(1,3-dichloro-2-propyl) phosphate (TDCPP) and Firemaster-550 in polyurethane foam to meet flammability standards[1,2]. TDCPP was recently added to the California Proposition 65 list as a chemical shown to cause cancer[3]. Relatively little toxicity data is available for Firemaster 550, a mixture of 2,3,4,5-tetrabromo-ethylhexylbenzoate (TBB), (2-ethylhexyl)tetrabromophthalate (TBPH), and organophosphate compounds[4].

To date, investigations of human exposure to flame retardants have focused on the general population with few studies of occupational groups. However, potentially high exposures may occur in subpopulations such as gymnasts. Gymnastics training facilities typically contain large volumes of polyurethane foam in landing mats and loose foam pits. Loose foam pits contain hundreds of 'pit cubes', each an approximately 20 cm^3 piece of polyurethane foam. We previously reported high levels of flame retardants in pit cubes and dust from one gym along with a model suggesting that some gymnasts may be highly exposed[5]. Since many gymnasts are young females of reproductive age, high exposure in this potentially vulnerable population could have considerable public health implications.

The objective of the present study was to determine if gymnasts have higher average concentrations of PentaBDE congeners in their serum compared to the general U.S. population and to further characterize concentrations of flame retardants in gym equipment, air, and dust.

Materials and methods

Participants. We recruited a sample of 11 female gymnasts from one gym with a loose foam pit in the Eastern United States. To be eligible for participation, gymnasts had to be older than 15 years in age, healthy and practice at least 3 hours/week. Participating gymnasts were 18−22 years old and had been gymnasts for the past 12−19 years. All had practiced at their current gym for 9 months to >3 years and reported that their previous gym also had a loose foam pit. The study protocol was approved by the Boston University Medical Center Institutional Review Board and each gymnast gave informed consent prior to participation.

Sample Collection. Collection of personal and environmental samples centered around one practice day during the spring of 2012. Active air samples were collected from two locations in the gym over a 75-hour period, beginning on Tuesday and ending approximately one hour after practice on Friday. Each gymnast completed a brief questionnaire regarding her personal characteristics, habits, and gymnastics history. Following practice, approximately 30-mL of blood were collected from each gymnast. Tubes of serum were allowed to coagulate at room temperature for 4 hours and centrifuged for 15 minutes at 1,000 x g, after which they were separated into aliquots and stored at -80°C. One dust sample was collected from each gymnastics apparatus (vault, beam, bars and floor) and from the loose foam pit. Samples were collected into a cellulose extraction thimble that was placed in the crevice tool attachment of a canister vacuum cleaner. Gymnastics equipment was non-destructively screened for brominated flame retardants using an InnvoX α-6500 portable x-ray florescence (XRF) analyzer operating in RoHS/WEEE mode with a 30-second test duration[6]. Samples of polyurethane foam were collected from the loose foam pit and one large landing mat for chemical analysis.

Chemical Analysis. The 2 air[7], 6 dust[1,2,8], and 3 foam[9] samples were analyzed for PBDEs and other flame retardants using gas chromatography/mass spectrometry operated in electron-capture negative-ionization mode as previously described. The 11 serum samples were processed using automatic fortification with internal standards as well as addition of formic acid and water for denaturation and dilution using a Gilson 215 liquid handler (Gilson Inc.; Middleton, WI) followed by solid phase extraction using a Rapid Trace (Caliper Life Sciences; Hopkinton, MA) modular SPE system. Analytical determination was preformed by gas chromatography isotope dilution high resolution mass spectrometry[10]. Co-extracted lipids were performed on a silica: silica/sulfuric acid column using the Rapid Trace equipment for automation. Serum samples were analyzed for the primary PentaBDE congeners (BDEs 17, 28, 47, 66, 85, 99, 100, 153, 154, and 183), as well as BDE 209, BB 153, 35 polychlorinated biphenyls (PCBs), and 9 organochlorine pesticides.

Data Analysis. Samples were blank-corrected on an analyte and congener-specific basis. Serum and dust concentration data were corrected using the average of the laboratory blanks. Method detection limits (MDLs) were calculated as 3 times the standard deviation of the blanks; MDLs for serum were sample size dependant. The laboratory instrument detection limit was used as the MDL when analytes were not detected in the blanks or there was insufficient data to calculate an MDL. Quantifiable concentrations < MDL were reported as the measured value, otherwise they were substituted with a value of MDL/2. Statistical analyses were preformed using SAS (version 9.1; SAS Institute Inc., Cary, NC). Data were not normally distributed; therefore non-parametric methods were used. ΣPentaBDE in foam, air, and dust was defined as the sum of BDEs 17−154, excluding congeners that had a detection frequency <60% (foam: BDE 71 and 116; air: BDE 30, 116, 119; dust: BDE 30, 71, 116, 119).

Results and discussion

Gymnastics Equipment. XRF measurements of gym equipment identified the highest concentrations of bromine in pit cubes (3-6% by weight), landing mats (3%), and sting mats (2%) (Table 1). Laboratory results confirmed the presence of PentaBDE (5%), TBB (1.6%), and TBPH (0.7%) in the pit cubes. We previously found similar levels of PentaBDE in pit cubes from another gym; as well as TDCPP (6-7%), TBB (3%), and TBPH (1%) in pit cubes obtained from a distributor. These data suggest that gym equipment containing polyurethane foam can contain high and variable levels of flame retardants.

Table 1. Percentage by weight levels of bromine in gym equipment measured by XRF.

Gym Equipment	Primary Gym		Another Gym[5]	
	n	GM (Range) %	n	GM (Range) %
Pit Cube	2	4.14 (3.16−6.16)	4	2.86 (0.48−5.60)
Landing Mat	15	0.66 (0.01−3.61)	0	NA
Sting Mat	7	0.26 (0.08−1.99)	1	0.53
Vault Runway Carpet	2	0.62 (0.55−0.69)	1	0.90
Above-ground Pit	3	0.01 (<0.01−0.05)	1	0.02
Vault Runway Foam	2	0.01 (0.01−0.02)	0	NA
Floor Carpet/Foam	4	<0.01	1	0.04−0.62

Air. Concentrations of ΣPentaBDE, TBB, and TBPH were 5−6 times higher in air near the loose foam pit than on the opposite side of the gym near the entrance, whereas spatial variability of TDCPP and TCPP were less pronounced (Table 2). Concentrations of PentaBDE in gym air were orders of magnitude higher than measured in Boston homes[7]. This is consistent with the high concentration of PentaBDE (15.2 ng/m^3) collected from a single Canadian gym using a passive sampler[11].

Table 2. Concentrations of flame retardants in gym air (ng/m^3).

Analyte	Near the Loose Foam Pit	Near the Gym Entrance
ΣPentaBDE	129	23.1
TBB	26.4	5.3
TBPH	17.0	2.8
TDCPP	11.1	7.3
TCPP	15.1	10.9

Dust. Concentrations of ΣPentaBDE, TBB, TBPH, and TDCPP were elevated in dust from the current gym compared to Boston area residences[1,2,12] (Table 3). We previously measured higher concentrations of these flame retardants in dust from another gym[5], suggesting levels can vary greatly between gyms.

Table 3. Concentrations of flame retardants in dust (μg/g).

Analyte	Current Gym Range (n=5)	Another Gym[5] Range (n=3)	Residence GM (Range)
ΣPentaBDE	93.1−1,780	591−2,670	5.46 (0.98−52.3)[12]
TPP	0.76−3.07	20.7−25.0	7.36 (<0.15−1800)[2]
TBB	20.8−85.6	<MDL−347	0.32 (<0.007−15.1)[2]
TBPH	17.3−118	<MDL−207	0.23 (0.003−10.6)[1]
TDCPP	2.84−22.8	3.19−38.2	1.89 (<0.09−56.1)[1]

Serum. BDEs 28, 47, 85, 99, 100, and 153 were detected in greater than 50% of gymnast serum samples (Table 4). Geometric mean (GM) concentrations of BDEs 47, 100, and 153 were significantly higher than levels in the general U.S. population as determined by the 2003/2004 National Health and Nutrition Examination Survey (NHANES) (ages 12 to >60)[13]. The same observation was made when compared to two other U.S. populations: a 2009 sample of office workers (ages 25 to 64) and a 2008−2010 sample of pregnant women (ages 18 to 39). In particular, the GM concentration of BDE 153 was 5.7 times higher among gymnasts than in the general population. GM concentrations of PBDEs were lower than an occupational study of foam recyclers and carpet installers, with the exception of BDE 153, which was slightly higher[14]. PentaBDE congeners 47, 85, 99, 100, and 154 were highly correlated with one another ($r_s>0.8$, $p<0.001$), moderately correlated with BDE 28 ($r_s>0.64$, $p<0.05$), and uncorrelated with BDE 153 ($r_s<0.4$, $p>0.2$).

Table 4. PBDEs (ng/g lipid) measured in serum from gymnasts and other U.S. Populations.

PentaBDE Congener	Gymnasts (n=11), 2012			U.S. Population[13] (n≈2000), 2003/4	Occupational[14] (n=15), 2006
	Detection Frequency	Range	GM (95% CI)	GM (95% CI)	GM (95% CI)
BDE 28	64%	<0.55 − 4.7	1.50 (0.94−2.39)	1.2 (1.0−1.4)	3.85 (2.36-6.28)
BDE 47	100%	15.6 − 189	43.5 (26.8−70.5)	20.5 (17.6−23.9)*	91.7 (54.9-153)
BDE 99	100%	4.1 − 70.6	11.9 (3.95−20.4)	5.0 (4.4−5.6)	27.1 (15.8-46.4)
BDE 100	100%	3.7 − 47.7	10.9 (6.80−17.4)	3.9 (3.4−4.5)*	20.8 (12.7-34.0)
BDE 85,155	55%	<0.65 − 5.9	1.43 (0.93−2.21)	not reported	2.70 (1.62-4.48)
BDE 153	100%	10.8 − 96.9	32.5 (20.5−51.5)	5.7 (5.1−6.3)*	27.4 (18.4-40.9)

*Significantly different from gymnast GM at the α=0.05 level.

Possible explanations for the proportionally high levels of BDE153 in gymnast serum include higher exposure or decreased elimination of BDE153 in relation to the other congeners. BDEs 47, 99, and 100 dominated dust and air samples, thus a disproportional higher exposure to BDE153 compared to other pentaBDE congeners in the gym is not likely. While the human half lives of PentaBDE congeners have not been directly measured, the half life for BDE 153 has been roughly estimated as 6-7 years vs. 1-3 years for BDE 47, 99, 100[15]. This long half life may explain the high concentrations of BDE 153 found in gymnast serum.

DDE and six PCB congeners (PCB 74, 118, 153, 138/158, 180, 170) were present at significantly lower GM concentrations (56.8, 2.05, 1.96, 5.13, 3.00, 3.63, 1.66 ng/g lipid) compared to the general U.S. population as determined by the 2003/2004 NHANES[16]. BDE 209 and BB 153 were not detected in any of the gymnast serum samples. These results suggest that the elevated concentrations of PentaBDE congeners in the gymnasts relative to the general US population was not due to differences in diet or other factors such as low adiposity.

Overall, these findings suggest that the gymnasts in this sample experienced high exposures to PentaBDE flame retardants and may also have high exposures to other chemicals used in polyurethane foam. We plan to engage the gymnastics community to identify effective communication and intervention strategies.

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