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Flame Retardant Exposure among Collegiate U.S. Gymnasts

Courtney C. Carignan[1,*], **Wendy Heiger-Bernays**[1], **Michael D. McClean**[1], **Simon C. Roberts**[2], **Heather M. Stapleton**[2], **Andreas Sjödin**[3], and **Thomas F. Webster**[1]

Courtney C. Carignan: courtney.c.carignan@dartmouth.edu; Wendy Heiger-Bernays: whb@bu.edu; Michael D. McClean: mmcclean@bu.edu; Simon C. Roberts: simon.roberts@duke.edu; Heather M. Stapleton: heather.stapleton@duke.edu; Andreas Sjödin: asjodin@cdc.gov; Thomas F. Webster: twebster@bu.edu

[1]Department of Environmental Health, Boston University School of Public Health, Boston, Massachusetts, USA

[2]Nicholas School of the Environment, Duke University, Durham, North Carolina, USA

[3]Division for Laboratory Sciences, National Center for Environmental Health, Centers for Disease Control and Prevention, Atlanta, Georgia, USA

Abstract

Gymnastics training facilities contain large volumes of polyurethane foam, a material that often contains additive flame retardants such as PentaBDE. While investigations of human exposure to flame retardants have focused on the general population, potentially higher than background exposures may occur in gymnasts and certain occupational groups. Our objectives were to compare PentaBDE body burden among gymnasts to the general U.S. population and characterize flame retardants levels in gym equipment, air and dust. We recruited 11 collegiate female gymnasts (ages 18–22) from one gym in the Eastern U.S. The geometric mean (GM) concentration of BDE-153 in gymnast sera (32.5 ng/g lipid) was 4–6.5 times higher than general U.S. population groups. Median concentrations of PentaBDE, TBB and TBPH in paired handwipe samples were 2–3 times higher after practice compared to before, indicating the gymnasts contacted these flame retardants during practice. GM concentrations of PentaBDE, TBB and TBPH were 1-3 orders of magnitude higher in gym air and dust than in residences. Our findings suggest that these collegiate gymnasts experienced higher exposures to PentaBDE flame retardants compared to the general U.S. population and that gymnasts may also have increased exposure to other additive flame retardants used in polyurethane foam such as TBB and TBPH.

Introduction

Flame retardants are chemical additives used to meet flammability standards for materials. PentaBDE is a mixture of polybrominated diphenyl ethers (PBDEs) that was widely used in polyurethane foam for furniture. Flame retardants escape from the polyurethane foam over time and accumulate in the air and dust of indoor environments[1,2]. PentaBDE congeners bioaccumulate and have human half-lives roughly estimated at 1–12 years[3]. They are endocrine disruptors that have been associated with subclinical changes in thyroid hormones in several epidemiologic studies[4,5] as well as reproductive impairments including reduced fecundability and failed embryo implantation[6,7]. Recent research has found associations between *in utero*/early childhood exposures and neurodevelopmental outcomes[8-11]. Due to concerns regarding its persistence and toxicity, PentaBDE was banned in the European Union in 2004 and phased out of production in the U.S in 2005.

*courtney.c.carignan@dartmouth.edu; Dartmouth College, 78 College St. HB6044, Hanover, New Hampshire 03755 USA.

SUPPORTING INFORMATION AVAILABLE. Tables S1-S4 and Figures S1-S2 are available free of charge via the Internet at http://pubs.acs.org.

Restrictions on the use of PentaBDEs have resulted in the increased use of other flame retardants such as tris(1,3-dichloro-2-propyl) phosphate (TDCPP) and Firemaster 550.[12,13] TDCPP is a suspected endocrine disruptor and was recently added to the California Proposition 65 list as a carcinogen[14]. A recent study of rats found increased serum thyroxine in dams exposed to Firemaster 550. Their offspring experienced advanced female puberty, male cardiac hypertrophy, weight gain and increased anxiety[15]. Firemaster 550 contains four components: triphenyl phosphate (TPP), 2-ethylhexyl-2,3,45-tetrabromobenzoate (TBB), bis(2-ethylhexyl)-2,3,4,5-tetrabromophthalate (TBPH) and a mixture of isopropylated triphenylphosphate isomers[16].

The general population of the U.S. and Canada has the highest sera concentrations of PentaBDEs, presumably because most of the PentaBDE produced was used in North America[17]. U.S. body burdens vary by gender, age, socioeconomic status and region with higher concentrations in males, teenagers, non-whites, and Californians[18,19]. Investigations of PentaBDE exposure have primarily focused on diet and indoor spaces such as homes, offices and vehicles[20-24]. Only one U.S. study has examined occupational exposure to PentaBDE, measuring serum levels among foam recyclers and carpet installers[25]. Some non-occupational populations may experience higher than general population exposures to flame retardants due to special uses of polyurethane foam. For example, gymnastics training facilities contain a large amount of polyurethane foam in equipment such as landing mats and loose foam pits. Our objectives were therefore to characterize PentaBDE body burden among gymnasts, compare results to the general U.S. population, and measure PentaBDE and other flame retardants in gym equipment, air, and dust.

Methods

Study Design

We recruited a convenience sample of 11 female gymnasts from one collegiate gym with a loose foam pit (Gym 1) 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. The Boston University Medical Center Institutional Review Board approved the study protocol and the involvement of the Centers for Disease Control and Prevention laboratory was determined not to be engaged in human subjects research. All participants gave their informed consent prior to participation. Each participant filled out a questionnaire regarding her personal characteristics, habits (such as handwashing, transportation, and diet), gymnastics history and gym use. Sampling centered around one Friday practice during the spring of 2012.

Serum

We collected approximately 30 mL of blood from each participant after a gymnastics practice. Blood was allowed to coagulate at room temperature for 4 hours, centrifuged for 15 minutes at 1,000 × g and stored at -80°C. Serum samples were analyzed for lipids, PBDEs and other persistent organic pollutants (POPs) including polychlorinated biphenyls (PCBs) and organochlorine pesticides using previously published methods[26,27]. TBB, TBPH, TPP, TCPP and TDCPP were not analyzed in serum. The sample processing method included automatic fortification with internal standards, followed by liquid/liquid extraction using a Gilson 215 liquid handler (Gilson Inc.; Middleton, WI). Removal of co-extracted lipids was performed on a silica: silica/sulfuric acid column using a Rapid Trace (Caliper Life Sciences; Hopkinton, MA) modular solid phase extraction (SPE) system. Analytical determination of the target analytes was performed by gas chromatography isotope dilution high resolution mass spectrometry as previously described[27] using a DFS (ThermoFinnigan MAT, Bremen, Germany) instrument.

Handwipes

Handwipe samples were collected immediately before and after practice, which lasted about 2.5 hours. Under the instruction and supervision of study personnel, each participant soaked a 7.6 cm^2 sterile gauze pad in 3 mL of isopropyl alcohol and wiped both of her own palms from wrist to fingertips. She then inserted the gauze pad into a clean glass vial, wrapped the vial in foil and bubble wrap, and placed the sample in a polyethylene zip bag. She repeated this process for the back of both her hands using a second handwipe kit. Samples were placed on ice and later stored at −20 °C. Study personnel collected three field blanks using the described protocol, while wearing nitrile gloves and without wiping hands Paired palms and back of hands handwipe samples were composited for extraction and analyzed together using gas chromatography negative chemical ionization mass spectrometry (GC/ECNI-MS) as previously described[28], with the following modifications. Following Soxhlet extraction with 50:50 DCM:Hexane, wipe extracts were concentrated to 1.0 ml in hexane and cleaned using SPE Florisil cartridges as previously described[29]. PBDEs, TBB and TBPH were eluted in Fraction 1 (hexane), while tris(1-chloro-isopropyl) phosphate (TCPP), TDCPP and TPP eluted in Fraction 2 (ethyl acetate). Deuterated TDCPP (dTDCPP) was used as an internal standard for TDCPP, a mono-fluorinated tetrabrominated diphenyl ether (F-BDE 69; Chiron, Trondheim, Norway) was used as an internal standard for tri-nonaBDEs, and ^{13}C BDE-209 was used as an internal standard for BDE-209.

Dust

We collected a total of five dust samples from Gym 1: one from each of the women's gymnastics apparatus (vault, bars, beam and floor) and one from within the loose foam pit. Samples were collected in a cellulose extraction thimble (Whatman International) inserted into the crevice tool of a Eureka Mighty-Mite canister vacuum cleaner (Model 3670)[1]. We sampled each apparatus by slowly drawing the crevice tool across the sampling area for approximately 10 minutes. We collected dust from the loose foam pit by entering the pit with the crevice tool and vacuuming for approximately 10 minutes. After collection, each thimble was wrapped in aluminum foil, sealed in a polyethylene bag, and stored at room temperature until processed. We collected field blanks by vacuuming sodium sulfate powder (as a surrogate for dust) off clean aluminum foil. Each dust sample was later passed through a 500 μm sieve. We cleaned all sampling equipment prior to sample collection[22]. Dust samples were extracted using the method reported in the previous section. Extracts were analyzed using GC/ECNI-MS as previously described[2,12,30]. Three dust samples from Gym 1 were found to contain flame retardant levels above the highest point of our calibration curve. Due to insufficient amount of dust for a re-analysis, the levels were extrapolated using a linear regression above the highest point of the calibration curve. All calibration curves had an R^2 value >0.999 using a linear regression fitting model.

Air

We collected air samples from Gym 1 using stationary air sampling pumps placed in two locations in the gym: 1) within 30 cm of the pit and 2) on the opposite side of the gym from the pit; this location was near the door of the gym that led into a larger building. Samples were collected over a continuous 75-hour period beginning prior to practice on Tuesday and ending after practice the following Friday. We calibrated each pump to a flow rate of 2 L/min for a total volume of about 9.5 m^3, with an average nominal change in flow of 0.2 L/min over the sampling period. Sampling media included a glass tube containing a glass fiber filter (pore size: 1 μm) followed by a pre-cleaned polyurethane foam plug, XAD-2 resin, and a second pre-cleaned polyurethane foam plug. The sampling medium was connected to each air pump via tygon tubing (0.64 cm) and mounted on a tripod approximately 1.2 m from the ground. Following collection, each sample was wrapped in aluminum foil, sealed in a polyethylene zip bag, and stored at -4°C prior to extraction. Field quality control included a duplicate sample from the near-pit sampling location and one field blank. Air samples were analyzed using GC/ECNI-MS as previously described[31].

Gymnastics Equipment

Concentrations of bromine in gymnastics equipment were non-destructively measured using an InnovX Alpha 6500 portable x-ray florescence (XRF) analyzer operating in RoHS/WEEE mode with 30-second test duration. In our applications, bromine concentrations in polyurethane foam measured via XRF correlates highly with concentrations of brominated flame retardants as measured by GC-ECNI/MS, but overestimates these concentrations by about 50%[1,16]. Bromine levels were measured in the foam of landing mats and pit cubes as well as the carpet and foam of the spring-loaded floor, springboards and vaulting runway. The loose foam pit was approximately 4.3 by 5.8 by 2.4-m and filled with pit cubes (each 20 cm^3). Gym management reported that pit cubes were added at two different time points, approximately 10 and 20 years prior to our sampling. One pit cube of each age was collected from the gym and later sub-sampled using a clean razor blade. Each foam sample was wrapped in foil and sealed in a polyethylene zip bag. Foam samples were analyzed using GC/ECNI-MS as previously described[1,12].

Additional gyms and pit cubes

We collected samples of dust and foam from a second gym (Gym 2) in the Eastern U.S. during the fall of 2010 using the methods described in the previous sections. We vacuumed dust from two locations: 1) within the loose foam pit and 2) from the surface of a landing mat that covered a small portion of the pit. We collected the gym vacuum cleaner bag that had been used in all areas of the gym including the office and lobby. The vacuum cleaner bag dust was sub-sampled using a clean plastic scoop, passed through a 500 μm sieve and handled like the other dust samples. We collected surface wipes from locations in both Gym 1 and Gym 2 (See SI for methods). We screened gym equipment for brominated flame retardants using XRF and collected four pit cubes, one of each age, from the loose foam pit. We obtained an additional pit cube from a third gym (Gym 3) in the Midwestern U.S. and purchased three new pit cubes from a distributor.

Scanning electron microscopy (SEM)

We investigated one dust sample and one pit cube from Gym 2 using SEM. Samples were mounted on an aluminum stub using 2-sided conductive carbon adhesive tape. Images were obtained at high vacuum at 30.0 eV using an FEI (Hillsboro, OR) XL30 environmental SEM with a Bruker (Billerica, MA) XFlash 4010 energy-dispersive x-ray spectroscopy detector to visualize the relative amounts of bromine ($K\alpha$=11.91 keV) and magnesium ($K\alpha$=1.25 keV) in 10 mm × 7.5 mm images (approximately 200× magnification).

Data Analysis

Serum analyte concentrations were adjusted for lipid content. Concentrations of flame retardants were blank-corrected on an analyte specific basis using the average of the laboratory (serum and dust data) or field blanks (wipe data). Air data were blank-corrected using the single field blank that was similar to concentrations measured in the two laboratory blanks. Recoveries were as follows: F-BDE69 averaged 102±20% (handwipes and dust) and 104±3% (air); ^{13}C BDE 209 averaged 97±16% (handwipes and dust); dTDCPP averaged 68±25% (handwipes and dust) and 82±6% (air) and dTPP averaged 50±2% (air). Method detection limits (MDLs) were calculated as 3 times the standard deviation of the laboratory blanks. The laboratory instrument detection limit was used as the MDL when analytes were not detected in the blanks or there were insufficient data to calculate an MDL. For calculation of geometric means and use in statistical tests, unquantified concentrations <MDL were substituted with MDL/2. We defined ΣPentaBDE as the sum of congeners detected in >50% of the serum, handwipe, air and dust samples: BDEs 28, 47, 85, 99, 100 and 153.

Concentrations of flame retardants in dust and serum were approximately log-normally (Shapiro-Wilk test) distributed for dust and serum. Accordingly, we log-transformed these data prior to analysis and report the geometric mean (GM) and geometric standard deviation (GSD). As handwipe levels were neither normally or log-normally distributed, we used the non-parametric signed rank test to compare paired handwipe samples. All statistical analyses were performed using SAS (version 9.1; SAS Institute Inc., Cary, NC) with statistical significance defined as $\alpha = 0.05$.

We identified six U.S. populations as comparison groups: office workers sampled in 2009 from the Boston, Massachusetts area (25–64 years old, n=31)[22]; pregnant women sampled in 2008–2010 from the Eastern U.S. (18–39 years old, n=137)[4]; the general U.S. population sampled in 2003-04 by the National Health and Nutrition Examination Survey (NHANES) (12–85 years old, n≈2000)[19]; U.S. teenagers (12-19 years old, n≈600)[19] and Californians (12–60^+ years old, n≈250)[18] subsampled from NHANES 2003-2004; and a 2006 occupational sample of adult foam recyclers and carpet installers (22-56 years old, n=15) with elevated sera concentrations of PentaBDEs[25]. To test the role of diet or other factors such as low adiposity, we compared sera concentrations of PCBs and organochlorine pesticides in gymnasts to U.S. teenagers and the general U.S. population[32], as diet is thought to be the primary exposure pathway for these POPs.

Results

Study population

Each participant had been a gymnast for at least 12 years, was a female of 18–22 years of age and currently trained at Gym 1. On average over the past year, participants reported training 19 hours/week during the competitive season (September–May) and 10 hours/week during the off-season (June-August). All trained at Gym 1 for the past 0.75–4 years and each confirmed that her previous gym had a loose foam pit.

Serum PBDEs

We detected BDEs 47, 99, 100, and 153 in all of the serum samples (Table 1). Detection frequencies of BDEs 28 and 85 were 64% and 55%, respectively. BDE-154 was detected in 45% of samples. BDEs 17, 66, 183 and 209 were below the MDL in all samples (Table S1). BDEs 47 and 153 were the dominant PentaBDE congeners in gymnast sera, comprising an average of 42 and 34% of ΣPentaBDE, respectively (Figure S1). Serum concentrations of PentaBDE congeners 47, 85, 99, 100, and 154 were highly correlated with one another (Pearson correlation coefficient $r>0.87$, $p<0.005$), moderately correlated with BDE-28 ($r>0.78$, $p<0.005$), and not correlated with BDE-153 ($r<0.41$, $p>0.2$). The PentaBDE congeners were not correlated with *p,p′*-dichlorodiphenyldichloroethylene (*p,p′*-DDE) or the PCBs ($r<0.31$, $p>0.2$).

The GM concentration of BDE-153 (32.5 ng/g lipid) in gymnast sera was comparable to occupationally exposed US foam recyclers and carpet installers, but 4–6.5 times higher than the five general population comparison categories: Boston office workers, pregnant women from the Eastern U.S., the general U.S. population, teenagers and Californians (Figure 1, Table S2). GM concentrations of BDEs 47, 99 and 100 in gymnast sera were 2–3 times higher than in office workers, pregnant women and the general U.S. population, but similar to teenagers and Californians. GM concentrations of BDEs 28, 47 and 99 in gymnast sera were significantly lower than in U.S. foam recyclers and carpet installers.

Serum POPs

We detected *p,p′*-DDE, the primary metabolite of dichlorodiphenyltrichloroethane (DDT), in 100% of gymnast sera; the remaining eight organochlorine pesticides had detection frequencies under 10% (Table S1). Of the 35 PCB congeners investigated, over half were below the MDL in all samples and only six had a detection frequency greater than 50%: PCBs 74, 118, 138/158, 153, 170 and 180. GM concentrations of these six PCB congeners were significantly lower in gymnast sera compared to the general U.S. population, but similar to U.S. teenagers (Figure 1, Table S2). The GM concentration of *p,p′*-DDE was significantly lower in gymnast sera compared to both the general U.S. population and teenagers.

Handwipes

Levels of ΣPentaBDE, TBB and TBPH were a median of 2.8, 2.2 and 2.8 times higher respectively, in handwipes collected after practice compared to before ($p<0.05$) (Table 2).

Dust

We detected PentaBDE, TBB, TBPH, TPP, TDCPP and TCPP in all measured dust samples (Table 3). PentaBDE was the dominant flame retardant in dust collected from all locations in both gyms. The highest concentrations of PentaBDE were collected from the balance beam of Gym 1 and from within the loose foam pit of Gym 2 (Table S3a). The highest concentrations of TBB and TBPH were from the balance beam and within the loose foam pit of Gym 1 and from the vacuum cleaner bag collected from Gym 2. Surface wipe samples also reflected higher loadings of ΣPentaBDE compared to the other measured flame retardants (Table S3b). No spatial variation with distance from the pit was observed.

Air

Concentrations of ΣPentaBDE, TBB, and TBPH in air were 5–6 times higher near the loose foam pit than on the opposite side of the gym near the entrance (Table 3). Concentrations of TPP, TDCPP and TCPP in air were almost twice as high near the loose foam pit compared to the opposite side of the gym. BDE-209, a PBDE congener not associated with the PentaBDE mixture, was detected at similar concentrations at the two locations.

Gymnastics Equipment

Using XRF, we identified percent (by weight) concentrations of bromine in pit cubes (3−6%), landing mats (0.005−3.6%), sting mats (0.8−2%) and the vault runway (0.5−0.9%) of both gyms (Table S4). We identified 0.6% bromine in the foam of the floor exercise in Gym 2. Both gyms had low or undetectable levels of bromine in the above-ground pits, spring-boards and carpet of the floor exercise area.

The GC/ECNI-MS results confirmed the presence of flame retardants in foam from all of the sampled pit cubes (Figure 2). One pit cube from Gym 1 contained PentaBDE and the other contained a mixture of TBB and TBPH. The pit cubes collected from Gym 2 and Gym 3 contained primarily PentaBDE. The pit cubes obtained from a distributor in 2010 contained either TDCPP or a mixture of TBB, TBPH and TPP. One pit cube purchased from a distributor (D-3) was advertised as lacking a fire retardant additive, but was found to contain 5.6% TDCPP. Proportions of PentaBDE congeners in the pit cubes, air and dust were similar to the PentaBDE technical mixture[33]. Consistent with previous work, XRF-measured

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bromine correlated highly (r_p=0.94) with brominated flame retardants measured via GC/ECNI-MS, overestimating the concentration by about 50% (Figure S2)[1,16].

Sem

We used SEM with energy dispersive x-ray spectroscopy to compare a pit cube containing PentaBDE (G2-1) to gym dust. Both were collected from within the pit of Gym 2. We observed bromine-containing branched structures in the pit cube and similar, fragmented structures in the dust (Figure 3). Some fragments were larger than 100 μm whereas others appeared much smaller. Magnesium-containing particulates were also visible in the gym dust and were likely gym chalk, which typically consists of magnesium carbonate.

Discussion

We identified higher than background concentrations of PentaBDEs in sera collected from 11 collegiate gymnasts in the Eastern U.S. The degree of elevation varied between PentaBDE congeners with a particularly high GM concentration of BDE-153 that is comparable to a sample of occupationally exposed foam recyclers and carpet installers[25]. The relatively low concentrations of BDEs 183 and 209 in gymnast sera is consistent with use patterns of the Octa or DecaBDE mixtures, which are not used in polyurethane foam. As the estimated half life of BDE-153 (6-12 years) is more than double that estimated for BDEs 47, 99 and 100 (1-3 years)[3], the higher levels of BDE-153 suggest that these gymnasts had higher exposures to PentaBDE in the past. This hypothesis is supported by the recent trend of Swedish breast milk samples, in which BDE-153 remained high as BDE-47 decreased[34]. Furthermore, the team coach reported that these collegiate gymnasts would have used loose foam pits more frequently in previous years when a greater proportion of their training time was spent learning new skills. It is plausible that PentaBDE would have been used in the pit cubes and landing mats in previous gyms.

An alternative explanation for the observed levels of PentaBDE in gymnast sera is a difference in diet or other factors such as low adiposity. We tested this by also measuring the gymnasts' serum concentrations of PCBs and organochlorine pesticides, as diet is thought to be the primary exposure pathway for these POPs, and comparing the results with the general U.S. population[32]. Most of these compounds were not detected in the gymnast sera or were measured at similar or significantly lower GM concentrations compared to U.S. teenagers and the general U.S. population. This result supports our primary hypothesis that the higher than background concentrations of PentaBDE in gymnast sera are due to exposures in the gym environment.

Previous work has shown that PentaBDE in dust and handwipes are important predictors of personal exposure[22,24]. Median concentrations of ΣPentaBDE in dust from Gyms 1 and 2 (371 and 951 μg/g) were three orders of magnitude higher than GM concentrations measured in Boston area homes, offices and vehicles (1.69−2.61 μg/g)[23]. Concentrations of PBDE congeners used in the Octa and DecaBDE mixtures were at least an order of magnitude lower than the PentaBDE congeners in the gym dust. This result is consistent with use patterns of these mixtures, which were not historically added to polyurethane foam. The median concentration of ΣPentaBDE in handwipes collected from the gymnasts after practice (348 ng) were three times higher than their before-practice handwipes (101 ng) or compared to the GM concentration of ΣPentaBDE in Boston office worker handwipes (70 ng)[22]. Allen et al. (2013) observed elevated concentrations of BDE-209 in airplane dust as well as in handwipes sampled after flights[35]. BDE-209 is a major component of the DecaBDE mixture, a PBDE mixture that is not used in polyurethane foam. The elevated concentrations of PentaBDE in gym dust and on handwipes likely contribute to the elevated concentrations measured in gymnast sera. Exposure during practice may be influenced by training activities between apparatus, gym chalk on skin and personal habits such as handwashing and hand-to-mouth behavior.

We identified high concentrations of bromine, an indicator of brominated flame retardants, in gymnastics equipment, particularly pit cubes and landing mats that had cloth or mesh coverings. Most of the pit cubes collected from the gyms contained PentaBDE. The microscopy analyses suggest that pit cubes physically degrade, a process that likely contributes to the high concentrations of PentaBDE in the dust. While volatilization is often thought of as the mechanism by which PentaBDEs get into indoor air and dust, our results suggest that physical breakdown (friability) of polymers can also be a mechanism, a route previously demonstrated for the much less volatile DecaBDE[36,37]. Low concentrations of bromine in some of the landing mats suggest that this equipment may also be acting as a sink for flame retardants in the gym[38].

Incidental ingestion of PentaBDE and other flame retardants in dust could occur via both hand-to-mouth activities and ingestion of fugitive dust. Hand-to-mouth behavior is an important exposure pathway for toddlers and may also be important for gymnasts who eat during or after practice[24]. Landing on the polyurethane foam pit cubes and mats may suspend inhalable dust particles. Although larger particulates (>10 μm) will not penetrate deep into the lung, they may still contribute to personal exposure upon being cleared by the mucociliary escalator and subsequently swallowed.

While inhalation is not considered a primary pathway of exposure to PentaBDE for the general U.S. population, it may be an important pathway for gymnasts: concentrations in the air of Gym 1 (20.4 and 120 ng/m^3) were orders of magnitude higher than in Boston area homes (GM=0.29 ng/m^3; Max=3.51 ng/m^3)[31]. The high gym air concentrations are consistent with those previously reported for a single Canadian gym using a passive sampler (15.2 ng/m^3)[39]. Dermal exposure to PentaBDE may also be higher for gymnasts compared to the general population due to several factors: 1) frequent contact with gym foam and dust, 2) a high proportion of exposed skin and 3) potentially increased dermal permeability due to sweat from physical exertion.

Gymnasts may also experience higher than background exposures to other flame retardants used in polyurethane foam such as TBB, TBPH, TPP and TDCPP. We identified these flame retardants in foam and dust from both gyms as well as in pit cubes ordered from a distributor. With the phase out of PentaBDE, use of these flame retardants and other PentaBDE replacements may have become more common in gymnastics equipment[13,16]. The relative importance of exposure via the ingestion, inhalation and dermal pathways may differ depending on physical properties of each flame retardant. Personal exposure to PentaBDE and other flame retardants may vary between gymnasts depending on the flame retardants present in their gym as well as personal factors such as the their training duration and activities, handwashing and bathing frequency, diet and exposure to sources in other microenvironments (e.g., vehicle, school, home).

An important strength of this study is the collection of an exposure biomarker coupled with measures of personal exposure, environmental media and sources in the gym environment. Measurement of other POPs in serum allowed us to test the potential role of diet and low adiposity on our results. A major limitation of this study is the small sample size. We did not have measurements from participants' previous gyms or information on specific gym activities during practice on the day of handwipe sampling. Our findings are not generalizable to all gymnasts, many of whom may train much less frequently. Nevertheless, this is the first study to investigate gymnasts as a potentially highly exposed and vulnerable population and demonstrates the need for further investigation.

Future research on gymnasts should include a larger sample size and seek to identify the primary exposure pathways to inform recommendations for reducing personal exposures. For example, increased handwashing has been associated with lower body burdens of PBDEs in office workers and may be an effective intervention strategy for gymnasts[22]. The importance of inhalation vs. incidental ingestion exposures for gymnasts could be clarified by improving our understanding of foam friability as well as size fractionation in gym air and dust.

Overall, our findings demonstrate that these collegiate gymnasts experienced higher exposures to PentaBDE flame retardants compared to the general U.S. population and suggest that gymnasts may have increased exposure to other additive flame retardants used in polyurethane foam. We found evidence that the polyurethane foam pit cubes and landing mats are a source of PentaBDE, TBB and TBPH to the gym environment. Despite the U.S. phase-out of PentaBDE production nearly a decade ago, large amounts are still in use. Furthermore, TBB, TBPH, TPP and TDCPP are being used as replacement flame retardants in newly manufactured pit cubes, suggesting the potential for increasing exposure to these compounds as older gym equipment is replaced. Additional research is needed to confirm these findings and improve our understanding of gymnast exposures.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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References

1. Allen JG, McClean MD, Stapleton HM, Webster TF. Linking PBDEs in house dust to consumer products using x-ray fluorescence. Environ Sci Technol. 2008; 42(11):4222–4228. [PubMed: 18589991]
2. Stapleton HM, Dodder NG, Offenberg JH, Schantz MM, Wise SA. Polybrominated diphenyl ethers in house dust and clothes dryer lint. Environ Sci Technol. 2005; 39(4):925–931. [PubMed: 15773463]
3. Geyer HJ, Schramm KW, Darnerud PO, Aune M, Feicht EA, Fried KW, Henkelmann B, Lenoir D, Schmid P, DMcDonald TA. Terminal elimination half-lives of the brominated flame retardants TBBPA, HBCD, and lower brominated PBDEs in humans. Organohalogen Compd. 2004; 66:3867–3872.
4. Stapleton HM, Eagle S, Anthopolos R, Wolkin A, Miranda ML. Associations between polybrominated diphenyl ether (PBDE) flame retardants, phenolic metabolites, and thyroid hormones during pregnancy. Environ Health Perspect. 2011; 119(10):1454–1459. [PubMed: 21715241]
5. Chevrier J, Harley KG, Bradman A, Gharbi M, Sjödin A, Eskenazi B. Polybrominated diphenyl ether (PBDE) flame retardants and thyroid hormone during pregnancy. Environ Health Perspect. 2010; 118(10):1444–1449. [PubMed: 20562054]
6. Johnson PI, Altshul L, Cramer DW, Missmer SA, Hauser R, Meeker JD. Serum and follicular fluid concentrations of polybrominated diphenyl ethers and in-vitro fertilization outcome. Environ Int. 2012; 45:9–14. [PubMed: 22572111]

7. Harley KG, Marks AR, Chevrier J, Bradman A, Sjödin A, Eskenazi B. PBDE concentrations in women's serum and fecundability. Environ Health Perspect. 2010; 118(5):699–704. [PubMed: 20103495]
8. Eskenazi B, Chevrier J, Rauch SA, Kogut K, Harley KG, Johnson C, Trujillo C, Sjödin A, Bradman A. In utero and childhood polybrominated diphenyl ether (PBDE) exposures and neurodevelopment in the CHAMACOS study. Environ Health Perspect. 2013; 121(2):257–262. [PubMed: 23154064]
9. Hoffman K, Adgent M, Goldman BD, Sjödin A, Daniels JL. Lactational exposure to polybrominated diphenyl ethers and its relation to social and emotional development among toddlers. Environ Health Perspect. 2012; 120(10):1438–1442. [PubMed: 22814209]
10. Gascon M, Fort M, Martinez D, Carsin AE, Forns J, Grimalt JO, Marina LS, Lertxundi N, Sunyer J, Vrijheid M. Polybrominated diphenyl ethers (PBDEs) in breast milk and neuropsychological development in infants. Environ Health Perspect. 2012; 120(12):1760–1765. [PubMed: 23052368]
11. Roze E, Meijer L, Bakker A, Van Braeckel K, Sauer PJJ, Bos AF. Prenatal exposure to organohalogens, including brominated flame retardants, influences motor, cognitive, and behavioral performance at school age. Environ Health Perspect. 2009; 117(12):1953–1958. [PubMed: 20049217]
12. Stapleton HM, Klosterhaus S, Eagle S, Fuh J, Meeker JD, Blum A, Webster TF. Detection of organophosphate flame retardants in furniture foam and U.S. house dust. Environ Sci Technol. 2009; 43(19):7490–7495. [PubMed: 19848166]
13. Stapleton HM, Sharma S, Getzinger G, Ferguson PL, Gabriel M, Webster TF, Blum A. Novel and high volume use flame retardants in US couches reflective of the 2005 PentaBDE phase out. Environ Sci Technol. 2012; 46(24):13432–13439. [PubMed: 23186002]
14. [accessed October 12, 2012] Chemicals known to the State to cause cancer or reproductive toxicity; State of California Environmental Protection Agency, Office of Environmental Health Hazard Assessment. Safe Drinking Water and Toxic Enforcement Act of 1986. Oct 28. 2011 http://oehha.ca.gov/prop65/prop65_list/newlist.html
15. Patisaul HB, Roberts SC, Mabrey N, McCaffrey KA, Gear RB, Braun J, Belcher SM, Stapleton HM. Accumulation and endocrine disrupting effects of the flame retardant mixture Firemaster® 550 in rats: an exploratory assessment. J Biochem Mol Toxic. 2013; 27(2):124–136.
16. Stapleton HM, Klosterhaus S, Keller A, Ferguson PL, van Bergen S, Cooper E, Webster TF, Blum A. Identification of flame retardants in polyurethane foam collected from baby products. Environ Sci Technol. 2011; 45(12):5323–5331. [PubMed: 21591615]
17. Hites RA. Polybrominated diphenyl ethers in the environment and in people: a meta-analysis of concentrations. Environ Sci Technol. 2004; 38(4):945–956. [PubMed: 14998004]
18. Zota AR, Rudel RA, Morello-Frosch RA, Brody JG. Elevated house dust and serum concentrations of PBDEs in California: unintended consequences of furniture flammability standards? Environ Sci Technol. 2008; 42(21):8158–8164. [PubMed: 19031918]
19. Sjödin A, Wong LY, Jones RS, Park A, Zhang Y, Hodge C, Dipietro E, McClure C, Turner W, Needham LL, Patterson DG. Serum concentrations of polybrominated diphenyl ethers (PBDEs) and polyhrominated biphenyl (PBB) in the United States population: 2003-2004. Environ Sci Technol. 2008; 42(4):1377–1384. [PubMed: 18351120]
20. Wu N, Herrmann T, Paepke O, Tickner J, Hale R, Harvey E, La Guardia M, McClean MD, Webster TF. Human exposure to PBDEs: associations of PBDE body burdens with food consumption and house dust concentrations. Environ Sci Technol. 2007; 41(5):1584–1589. [PubMed: 17396645]
21. Fraser AJ, Webster TF, McClean MD. Diet contributes significantly to the body burden of PBDEs in the general US population. Environ Health Perspect. 2009; 117(10):1520–1525. [PubMed: 20019900]
22. Watkins DJ, McClean MD, Fraser AJ, Weinberg J, Stapleton HM, Sjödin A, Webster TF. Exposure to PBDEs in the office environment: evaluating the relationships between dust, handwipes, and serum. Environ Health Perspect. 2011; 119(9):1247–1252. [PubMed: 21715243]
23. Watkins DJ, McClean MD, Fraser AJ, Weinberg J, Stapleton HM, Sjödin A, Webster TF. Impact of dust from multiple microenvironments and diet on PentaBDE body burden. Environ Sci Technol. 2012; 46(2):1192–1200. [PubMed: 22142368]

24. Stapleton HM, Eagle S, Sjödin A, Webster TF. Serum PBDEs in a North Carolina toddler cohort: associations with handwipes, house dust, and socioeconomic variables. Environ Health Perspect. 2012; 120(7):1049–1054. [PubMed: 22763040]
25. Stapleton HM, Sjödin A, Jones RS, Niehser S, Zhang Y, Patterson DG. Serum levels of polybrominated diphenyl ethers (PBDEs) in foam recyclers and carpet installers working in the United States. Environ Sci Technol. 2008; 42(9):3453–3458. [PubMed: 18522133]
26. Jones R, Edenfield E, Anderson DR, Zhang Y, Sjödin A. Semi-automated extraction and cleanup method for measuring persistent organic pollutants in human serum. Organoalogen Compd. 2012; 74:97–98.
27. Sjödin A, McGahee EE, Focant J, Jones RS, Lapeza CR, Zhang YL, Patterson DG. Semiautomated high-throughput extraction and cleanup method for the measurement of polybrominated diphenyl ethers and polybrominated and polychlorinated biphenyls in breast milk. Anal Chem. 2004; 76(15):4508–4514. [PubMed: 15283595]
28. Stapleton HM, Kelly SM, Allen JG, McClean MD, Webster TF. Measurement of polybrominated diphenyl ethers on hand wipes: estimating exposure from hand-to-mouth contact. Environ Sci Technol. 2008; 42(9):3329–3334. [PubMed: 18522114]
29. van den Eede N, Dirtu AC, Neels H, Covaci A. Analytical developments and preliminary assessment of human exposure to organophosphate flame retardants from indoor dust. Environ Int. 2011; 37(2):454–461. [PubMed: 21176966]
30. Stapleton HM, Allen JG, Kelly SM, Konstantinov A, Klosterhaus S, Watkins D, McClean MD, Webster TF. Alternate and new brominated flame retardants detected in US house dust. Environ Sci Technol. 2008; 42(18):6910–6916. [PubMed: 18853808]
31. Allen JG, McClean MD, Stapleton HM, Nelson JW, Webster TF. Personal exposure to polybrominated diphenyl ethers (PBDEs) in residential indoor air. Environ Sci Technol. 2007; 41(13):4574–4579. [PubMed: 17695899]
32. Patterson DG, Wong LY, Turner WE, Caudill SP, Dipietro ES, McClure PC, Cash TP, Osterloh JD, Pirkle JL, Sampson EJ, Needham LL. Levels in the US population of those persistent organic pollutants (2003-2004) included in the Stockholm Convention or in other long-range transboundary air pollution agreements. Environ Sci Technol. 2009; 43(4):1211–1218. [PubMed: 19320182]
33. La Guardia MJ, Hale RC, Harvey E. Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures. Environ Sci Technol. 2006; 40(20):6247–6254. [PubMed: 17120549]
34. Fangstrom B, Athanassiadis L, Odsjo T, Noren K, Bergman A. Temporal trends of polybrominated diphenyl ethers and hexabromocyclododecane in milk from Stockholm mothers, 1980-2004. Mol Nutr Food Res. 2008; 52(2):187–193. [PubMed: 18186105]
35. Allen AG, Stapleton HM, Vallarino J, McNeely E, McClean MD, Harrad SJ, Rauert CB, Spengler JD. Exposure to flame retardant chemicals on commercial airplanes. Environ Health. 2013; 12(17)
36. Webster TF, Harrad S, Millette JR, Holbrook RD, Davis JM, Stapleton HM, Allen JG, McClean MD, Ibarra C, Abdallah MAE, Covaci A. Identifying transfer mechanisms and sources of decabromodiphenyl ether (BDE 209) in indoor environments using environmental forensic microscopy. Environ Sci Technol. 2009; 43(9):3067–3072. [PubMed: 19534115]
37. Suzuki G, Kida A, Sakai S, Takigami H. Existence state of bromine as an indicator of the sourece of brominated flame retardants in indoor dust. Environ Sci Technol. 2009; 43(45):1437–42. [PubMed: 19350916]
38. Zhang X, Diamond ML, Ibarra C, Harrad S. Multimedia modeling of polybrominated diphenyl ether emissions and fate indoors. Environ Sci Technol. 2009; 43(8):2845–2850. [PubMed: 19475960]
39. Zhang X, Diamond ML, Robson M, Harrad S. Sources, emissions, and fate of polybrominated diphenyl ethers and polychlorinated biphenyls indoors in Toronto, Canada. Environ Sci Technol. 2011; 45(8):3268–3274. [PubMed: 21413794]

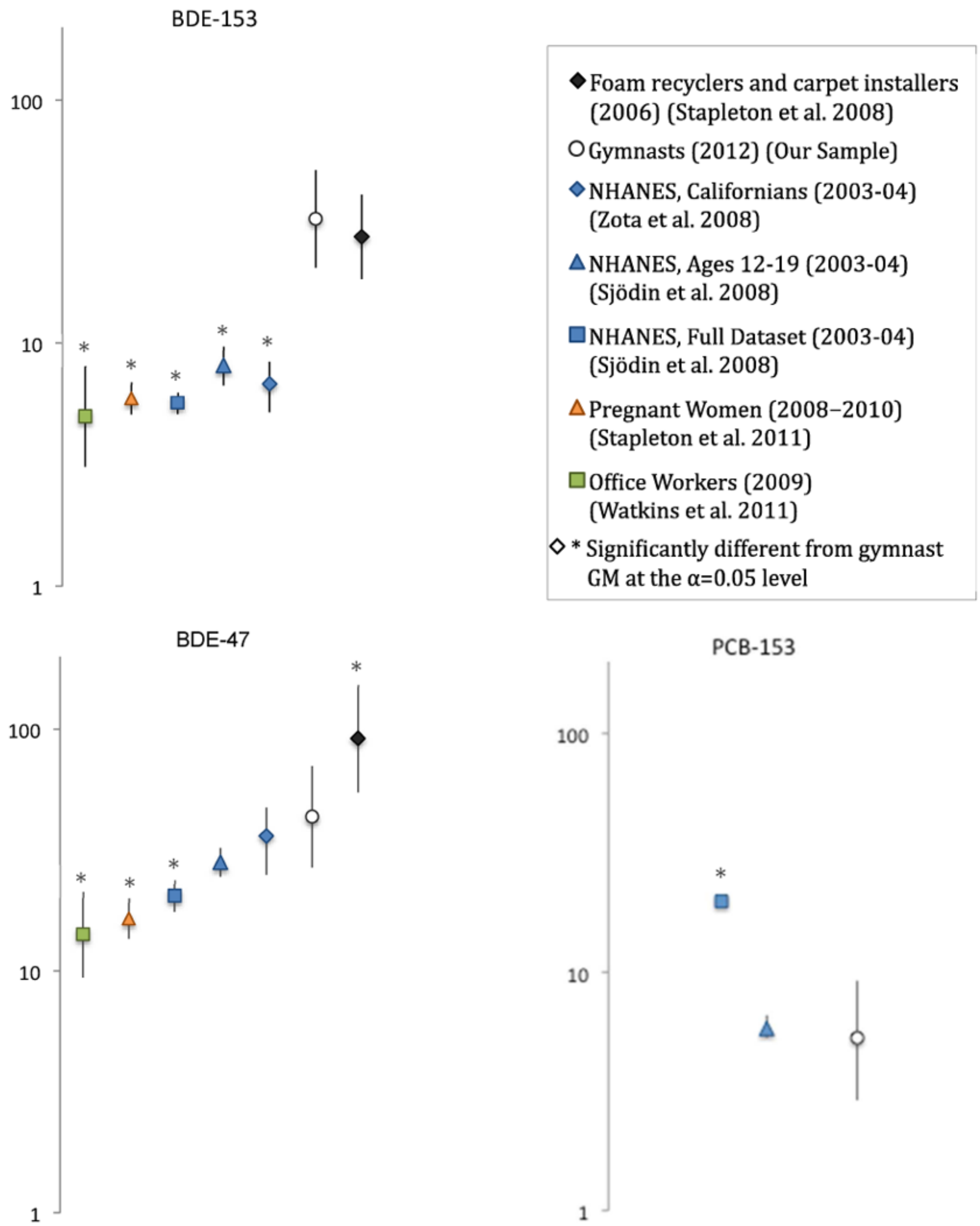

Figure 1.

Comparison of geometric mean (GM) concentrations of BDE-47, BDE-153 and PCB-153 in gymnast serum to other U.S. populations (ng/g lipid). Error bars indicate 95% confidence intervals around the GM.

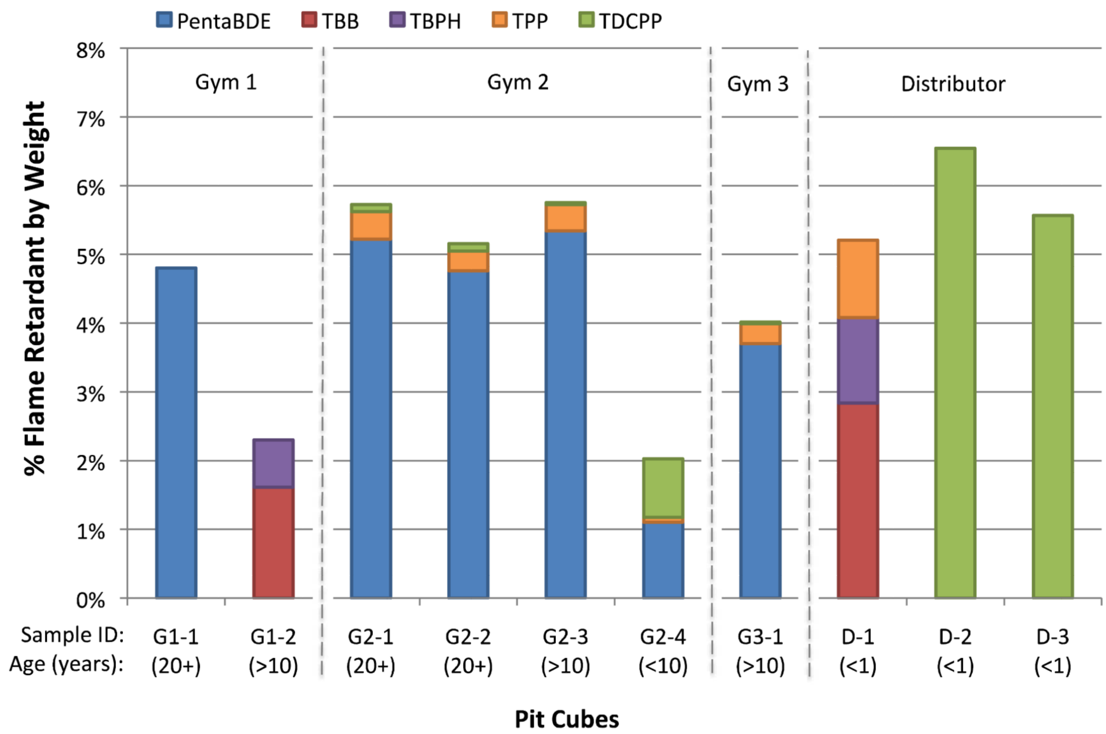

Figure 2.
Flame retardants identified in pit cubes.

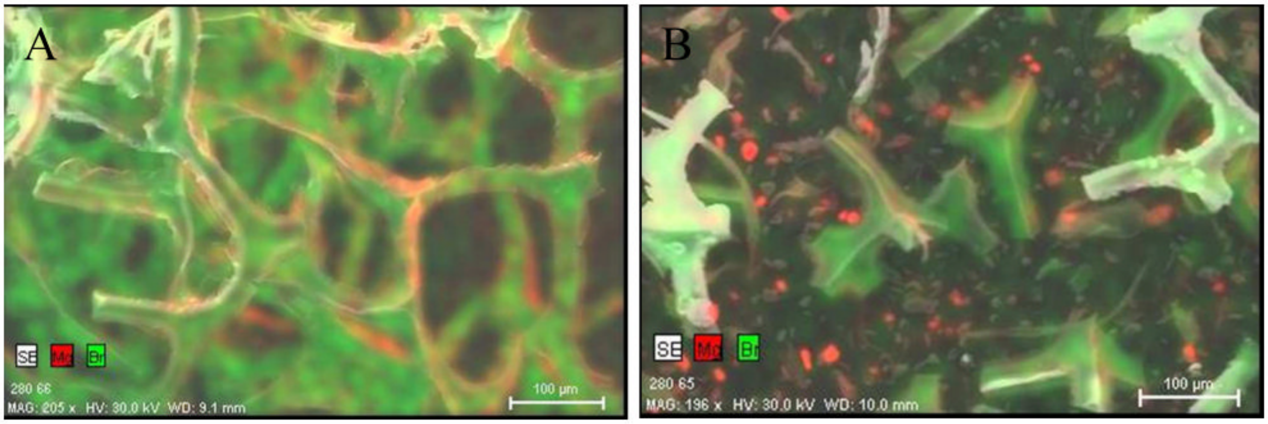

Figure 3.
Image created using scanning electron microscopy with energy dispersive x-ray spectroscopy of A) pit cube and B) dust collected from within the pit of Gym 2. The presence of bromine and magnesium are indicated by green and red, respectively.

Table 1

PentaBDEs measured in gymnasts serum (ng/g lipid).

Gymnast	BDE-28	BDE-47	BDE-85	BDE-99	BDE-100	BDE-153	ΣPentaBDE
1	<1.3	16.7	<1.3	5.5	3.7	15.6	42.8
2	1.5	27.5	<1.4	8.2	5.9	17.6	61.6
3	<1.1	36.3	1.3	11.2	9.7	18.8	77.9
4	<2.2	40.7	<2.2	9.1	9.4	27.2	88.7
5	1.7	36.8	<1.4	8.3	7.5	37.4	92.8
6	2.1	46	1.4	7.8	17.1	46.4	121
7	<1.3	15.6	<1.3	4.1	5.8	96.9	124
8	1.6	48.6	1.6	14	15.8	48.6	130
9	3.3	83.4	2.3	23	12.9	10.8	136
10	2.5	76.6	2.6	24.7	17.4	50.1	174
11	4.7	189	5.9	70.6	47.7	68.8	387
Freq. Det.	64%	100%	55%	100%	100%	100%	NA
GM (GSD)	1.50 (2.0)	43.5 (2.1)	1.43 (1.9)	12.0 (2.2)	10.9 (2.0)	32.5 (2.0)	111 (1.8)
Range	<1.1–4.7	15.6–189	<1.3–5.9	4.10–70.6	3.70–47.7	10.8–96.9	42.8–387
General US Population[2]							
GM	1.2	20.5	NR	<5.0	3.9	5.7	38.6

GM=geometric mean, GSD=geometric standard deviation; NR=not reported; NA=not applicable.

[1] ΣPentaBDE includes BDEs 28, 47, 85, 99, 100 and 153 which were detected in >50% of samples. BDE154 was detected in 45% of samples with a maximum of 6.8 ng/g lipid. BDEs 17, 66, 183 and 209 were not detected in any of the samples (Table S1).

[2] Sjödin et al. 2008. GM and 95% CIs for all comparison populations can be found in the Supporting Information, Table S2.

Table 2

Amounts of flame retardants (ng/wipe) in handwipe samples collected before and after practice.

	Before Practice		After Practice		
Analyte	**Detection Frequency**	**Median (Range)**	**Detection Frequency**	**Median (Range)**	**Median Change from before to after (p-value)**
PBDEs					
BDE 28, 83	27%	NR (<0.30-1.25)	64%	1.07 (<0.30-6.83)	NR
BDE 47	100%	38.6 (7.56-115)	100%	117 (19.4-1122)	71.2 (0.05)*
BDE 85, 155	55%	1.63 (<1.10-4.53)	73%	3.68 (<1.10-75.1)	3.12 (0.10)
BDE 99	82%	49.5 (<14.3-110)	100%	168 (22.2-1702)	104 (0.09)
BDE 100	64%	7.89 (<3.04-17.4)	100%	27.7 (3.31-297)	19.1 (0.32)
BDE 153	55%	3.56 (<2.08-8.26)	82%	11.7 (<2.08-154)	8.1 (0.10)
ΣPentaBDE	NA	101 (18.0-251)	NA	348 (46.6-3356)	234 (0.03)*
BDE 209	55%	5.00 (<4.34-13.5)	45%	NR (<4.34-9.31)	NR
Firemaster 550					
TBB	100%	60.8 (8.05-651)	100%	222 (34.9-770)	152 (0.04)*
TBPH	91%	27.9 (<3.19-264)	100%	96.4 (15.5-416)	70.8 (0.01)*
Organophosphates					
TDCPP	45%	NR (<31.8-255)	10%	NR (<31.8-81.9)	NR
TCPP	36%	NR (<40.2-97.4)	0%	NR (<40.2)	NR

NA=not applicable; NR= data not reported: detection frequency <50%.

* Statistically significant at the α=0.05 level using the signed rank test.

Table 3

Concentrations of flame retardants in air and dust.

	Air (ng/m^3)		Dust (μg/g)		
	Gym 1		Gym 1 (n=5)	Gym 2 (n=3)	Residences
Analyte	Near the Pit	Away from Pit	Median (Range)	Median (Range)	GM (Range)
PBDEs					
BDE 28, 83	1.43	0.68	0.91 (0.2–3.4)	5.66 (1.43–48.5)	0.014 (<0.001–0.38)[2]
BDE 47	44.9	9.99	98.8 (20.4–453)[1]	247 (146–390)	0.671 (<0.004–26.1)[2]
BDE 85, 155	2.24	0.31	11.2 (2.4–50.3)	79.1 (26.7–258)	0.033 (<0.001–4.26)[2]
BDE 99	56.6	7.58	208 (51.3–870)[1]	336 (222–518)	0.647 (<0.009–43.3)[2]
BDE 100	9.92	1.27	32.5 (7.92–194)[1]	145 (72.3–353)	0.135 (<0.002–12.5)[2]
BDE 153	4.79	0.58	19.5 (5.21–89.4)[1]	138 (56.1–367)	0.066 (<0.001–8.93)[2]
ΣPentaBDE	120	20.4	371 (87.4–1660)	951 (524–1940)	1.69 (0.009–91.0)[2,3]
BDE 183	0.10	<MDL	0.85 (0.44–1.87)	7.15 (1.90–47.2)	0.028 (0.002-0.229)[4]
BDE 209	0.33	0.45	5.21 (0.77–54.0)	2.50 (1.72–41.7)	4.50 (0.79–185)[4]
Firemaster 550					
TBB	26.1	5.01	28.9 (20.8–85.6)	0.01 (<0.001–0.35)	0.32 (<0.007–15.1)[5]
TBPH	16.9	2.66	30.0 (17.3–44.9)	0.06 (<0.001–0.21)	0.23 (0.003–10.6)[5]
Organophosphates					
TPP	80.2	40.5	NA	22.9 (20.1–25.0)	7.36 (<0.15–1800)[5]
TDCPP	12.5	8.41	5.05 (2.72–22.7)	13.0 (3.19–38.2)	1.89 (<0.09–56.1)[5]
TCPP	2.68	0.74	2.48 (0.75–3.06)	NA	0.57 (<0.14–5.49)[5]

MDL=method detection limit; NA=data not available

[1] May be less exact due to extrapolation from the end of a calibration curve.

[2] Watkins et al. 2012, dust collected in 2009 from the main living area of Boston area homes (n=31).

[3] ΣPentaBDE does not include BDE 85, 155.

[4] Allen et al. 2008, dust collected in 2006 from the main living area of Boston area homes (n=19).

[5]Stapleton et al. 2009, vacuum cleaner bags collected in 2002-2007 from Boston area homes (n=50).