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Urinary biomarkers of flame retardant exposure among collegiate U.S. gymnasts

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ABSTRACT

Flame retardants are widely used in polyurethane foam materials including gymnastics safety equipment such as pit cubes and landing mats. We previously reported elevated concentrations of flame retardants in the air and dust of a U.S. gymnastics training facility and elevated PentaBDE in the serum of collegiate gymnasts. Our objective in this pilot study was to compare urinary biomarkers of exposure to other flame retardants and additives of polyurethane foam including tris(1,3-dichloro-2-propyl) phosphate (TDCIPP), triphenyl phosphate (TPHP) and 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB) in samples collected from 11 collegiate gymnasts before and after a gymnastics practice (n = 53 urine samples total). We identified a 50% increase in the TPHP biomarker (p = 0.03) from before to after practice, a non-significant 22% increase in the TDCIPP biomarker (p = 0.14) and no change for the EH-TBB biomarker. These preliminary results indicate that the gymnastics training environment can be a source of recreational exposure to flame retardants. Such exposures are likely widespread, as we identified flame retardants in 89% of foam samples collected from gyms across the U.S.

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1. Introduction

Flame retardants are chemical additives used to meet flammability standards required for various types of materials including polyurethane foam (PUF). They are ubiquitous in the indoor environment due to their use in consumer products such as upholstered furniture as they are not chemically bonded to PUF and migrate into the air and dust of indoor environments (Allen et al., 2008; Stapleton et al., 2009). PentaBDE is a flame retardant mixture of polybrominated diphenyl ethers (PBDEs) that was used widely in PUF until concerns regarding its persistence and toxicity caused it to be banned in the European Union (in 2004) and phased out of production in the U.S. (in 2005). Flame retardants that replaced PentaBDE in foam include Firemaster® 550 (FM550) and tris(1,3-dichloro-2-propyl)phosphate (TDCIPP)

(Stapleton et al., 2012). FM550 is a mixture of brominated and phosphorylated compounds: triphenyl phosphate (TPHP), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), bis(2-ethylhexyl)-2,3,4,5-tetrabromophthalate (BEH-TEBP) and a mixture of isopropylated triphenylphosphate isomers (Stapleton et al., 2009) (abbreviations in this manuscript are as described in Bergman et al. (2012)). While TPHP is part of the FM550 mixture it can also be used in PUF with the PentaBDE mixture as well as in a variety of applications as a plasticizer (WHO Environmental Health Criteria, 2014).

The primary metabolites of these compounds are excreted primarily in urine as diphenyl phosphate (DPHP), bis(1,3-dichloro-2-propyl) phosphate (BDCIPP) and tetra-bromo benzoic acid (TBBA), respectively (Table A1 of Appendix I) (Lynn et al., 1982; Nomeir et al., 1981; Silva et al., 2016; Van den Eede et al., 2013). High frequencies of detection for these urinary metabolites among U.S. adults suggest that exposure to TDCIPP and components of the FM550 mixture is widespread (Butt et al., 2014; Hoffman et al., 2014). While the human half-lives of the PentaBDE congeners are estimated to be on the order of years (Trudel et al., 2010), the human half-lives of TPHP, TDCIPP and EH-TBB are not known but are likely on the order of hours based on animal studies (Hoffman et al., 2014; Nomeir et al., 1981; Sasaki et al., 1984; Van den Eede et al., 2013). We did not attempt to measure a biomarker for BEH-TEBP as a major metabolite has yet to be detected in urine or serum (Silva et al., 2016).

TDCIPP and components of the FM550 mixture are endocrine disrupting chemicals that can disrupt thyroid hormone action in the

Abbreviations: BDCIPP, bis(1,3-dichloro-2-propyl) phosphate; DPHP, diphenyl phosphate; EH-TBB, 2-ethylhexyl-2,3,4,5-tetrabromobenzoate; FM550, Firemaster® 550; MDL, method detection limit; MPP, methylated phenyl phosphates; PBDE, polybrominated diphenyl ether; PUF, polyurethane foam; SG, specific gravity; TBBA, tetra-bromo benzoic acid; TBPP, tris-isobutylated triphenyl phosphate; TCPP, tris(1-chloro-2-propyl) phosphate; TDCIPP, tris(1,3-dichloro-2-propyl) phosphate; TPHP, triphenyl phosphate.

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body (Farhat et al., 2013; Meeker and Stapleton, 2010; Patisaul et al., 2013; Wang et al., 2013). Dams exposed to the FM550 mixture had increased serum concentrations of thyroxine (T_4), while their offspring experienced advanced puberty (in females), cardiac hypertrophy (in males), significant weight gain (both sexes) and increased anxiety (Patisaul et al., 2013). TPHP, a component of the FM550 mixture, is a suspected obesogen as it can initiate adipocyte differentiation by binding and activating PPAR γ , a nuclear receptor that regulates fatty acid storage and glucose metabolism, and can also antagonize osteogenesis (Pillai et al., 2014). The brominated components of FM550, EH-TBB and BEH-TEBP, can adversely affect fecundity, as suggested by *in vitro* studies that found decreased cumulative egg production among exposed Japanese medaka (Saunders et al., 2014) and increased multinucleated germ cells in exposed fetal rat testes (Springer et al., 2012). In addition to its impact on circulating levels of thyroxine, TDCIPP is considered a genotoxic carcinogen by the State of California (CalEPA, 2015), and it is a suspected neurotoxicant that was found to have similar or greater potency as the developmental neurotoxicant organophosphate pesticide chlorpyrifos when tested in PC12 cell lines (Dishaw et al., 2011), an experimental model (Grandjean and Landrigan, 2014; Song et al., 1998).

To protect gymnasts from falls, gymnastics training facilities rely on safety equipment containing PUF, such as landing mats and the loose foam pit. We previously reported elevated concentrations of PentaBDE congeners, particularly BDE153, in the serum of 11 collegiate U.S. gymnasts compared to the general U.S. population (Carignan et al., 2013). The loose foam pit, a landing area used for learning new skills safely, was identified as a source of PentaBDE to the gym environment as components of the PentaBDE mixture were found in foam from the loose foam pit and elevated concentrations were measured in the air and dust of the gym. Additionally, hand-wipes collected after practice contained higher concentrations of the PentaBDE congeners compared to those collected before practice.

Similar to PentaBDE, the loose foam pit appeared to be a source of exposure to components of the FM550 mixture (i.e., TPHP and EH-TBB), which were identified at elevated concentrations in air and dust of the gym and in foam from the loose foam pit (Carignan et al., 2013). TDCIPP was not identified in foam from the loose foam pit but may have been in other foam equipment (i.e., landing mats) as it was present in gym air and dust at concentrations similar to other indoor environments (Carignan et al., 2013). While our previous study provided serum measurements of the PentaBDE congeners among gymnasts as a biomarker of internal dose, we did not report biomarkers of exposure to these other flame retardants.

Therefore, the objective of this pilot study was to measure urinary metabolites of TPHP, EH-TBB and TDCIPP in samples collected from the same 11 collegiate gymnasts before and after a gymnastics practice. We hypothesized that samples collected after practice would have higher concentrations of urinary metabolites compared to those collected before practice.

2. Methods

2.1. Study design

As previously reported, 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 (Carignan et al., 2013). To be eligible for participation, gymnasts had to be older than 15 years in age and practice at least 3 h/week. The Boston University Medical Center Institutional Review Board approved the study protocol. All participants gave their informed consent prior to participation. Sampling centered around one Friday practice during the spring of 2012. Prior to practice, each participant filled out a questionnaire regarding her demographics, habits, gymnastics history and gym use.

2.2. Urine

Each participant provided a sample of urine before (~2 pm) and soon after (~4:45 pm) practice as well as from her next three urinations. Urine samples were immediately placed in a cooler with ice for storage and transport. Upon receipt, samples were cold and ice packs were still frozen. Three field blanks were collected by transferring deionized water from one urine cup to another at the location of sample collection. Samples were measured for specific gravity (SG) and stored at $-20\text{ }^\circ\text{C}$ within 24 h of collection.

Urine samples were analyzed for DPHP, BDCIPP and TBBA using previously published methods (Cooper et al., 2011; Hoffman et al., 2014). Briefly, BDCIPP and DPHP were extracted and cleaned up with solid phase extraction StrataX-AW (60 mg, 3 mL, Phenomenex, Torrance, CA, USA). Deuterated BDCIPP (d10-BDCIPP) and d10-DPHP were spiked as the surrogate standard to quantify BDCIPP and DPHP, respectively. BDCIPP and DPHP extracted from urine were analyzed by LC/MS-MS (Agilent 6410 Triple Quad LCMS). Chromatographic separation of the extracts (5 μL injection) was performed on a Kinetex XBC18 column (100 \times 2.1 mm; 2.6 μm ; Phenomenex) maintained at 45 $^\circ\text{C}$. BDCIPP and DPHP were detected by atmospheric pressure chemical ionization (APCI) operating in negative ionization mode using multiple reaction monitoring (MRM).

A standard of TBBA was synthesized by the Small Molecule Synthesis Facility at Duke University (Durham, NC). Urine samples were analyzed for TBBA as previously described (Sasaki et al., 1984). Briefly, 10 mL urine samples were extracted with a novel liquid-liquid extraction technique using hexane and analyzed by LC/MS-MS in negative ESI (electrospray ionization) mode using MRM. The separation was performed using a Synergi Polar-RP column (50 \times 2.0 mm, 2.5 μm particle size, Phenomenex). 2,3,5-triiodobenzoic acid (TIBA, Sigma-Aldrich, St. Louis, MO) was used as the internal standard. In a matrix spike recovery evaluation, the average recovery of TBBA was $79 \pm 9\%$ in 10 urine samples. The method detection limit (MDL) of DPHP of 0.106 $\mu\text{g/L}$ was calculated as 3 times the standard deviation of the laboratory blanks; the average concentration of DPHP in these blanks was 0.131 $\mu\text{g/L}$ (0.10 to 0.19 $\mu\text{g/L}$). BDCIPP and TBBA were not detected in field or laboratory blanks, therefore their MDLs of 0.01, and 0.003 $\mu\text{g/L}$, respectively, were estimated using the instrument detection limit.

2.3. Pit Cube Survey

Between September 2014 and May 2015 we collected samples of pit cube foam from U.S. gymnastics training facilities and screened them for the presence or absence of 7 common flame retardants found in PUF through a testing service provided by the Duke University Superfund Research Center (Duke Superfund Analytical Chemistry Core Website, 2016). The protocol was approved by the Duke University Institutional Review Board. Participants were asked to cut a small piece of foam (about the size of a marble) from the pit cube, wrap in aluminum foil and seal in a zip bag and to indicate the approximate year of purchase. Samples were tested using GC-MS under previously published methods (Stapleton et al., 2011; Stapleton et al., 2012) for the presence or absence of seven different types of flame retardant chemicals that are commonly applied to polyurethane foam including PentaBDE, components of Firemaster @ 550 (FM550; containing TPHP, a mixture of isopropylated aryl phosphates, EH-TBB and BEH-TEBP), TDCIPP, tris(1-chloro-2-propyl) phosphate (TCPP), tris-isobutylated triphenyl phosphate (TBPP), a mixture of methylated phenyl phosphates (MPP) and V6. Field and laboratory blanks were prepared during sample preparation. All the data generated were background noise corrected using field blank samples. Positive detection of a flame retardant was defined as $>0.1\%$ by weight. Each participant received the results for his/her own sample(s), as well as an information sheet on common flame retardants found in furniture.

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