

## Flame Retardant Applications in Camping Tents and Potential Exposure

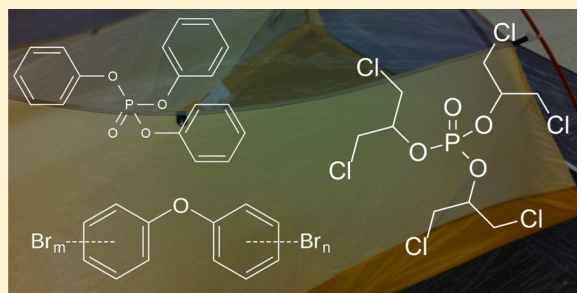
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### Supporting Information

**ABSTRACT:** Concern has mounted over health effects caused by exposure to flame retardant additives used in consumer products. Significant research efforts have focused particularly on exposure to polybrominated diphenyl ethers (PBDEs) used in furniture and electronic applications. However, little attention has focused on applications in textiles, particularly textiles meeting a flammability standard known as CPAI-84. In this study, we investigated flame retardant applications in camping tents that met CPAI-84 standards by analyzing 11 samples of tent fabrics for chemical flame retardant additives. Furthermore, we investigated potential exposure by collecting paired samples of tent wipes and hand wipes from 27 individuals after tent setup. Of the 11 fabric samples analyzed, 10 contained flame retardant additives, which included tris(1,3-dichloroisopropyl) phosphate (TDCPP), decabromodiphenyl ether (BDE-209), triphenyl phosphate, and tetrabromobisphenol-A. Flame retardant concentrations were discovered to be as high as 37.5 mg/g (3.8% by weight) in the tent fabric samples, and TDCPP and BDE-209 were the most frequently detected in these samples. We also observed a significant association between TDCPP levels in tent wipes and those in paired hand wipes, suggesting that human contact with the tent fabric material leads to the transfer of the flame retardant to the skin surface and human exposure. These results suggest that direct contact with flame retardant-treated textiles may be a source of exposure. Future studies will be needed to better characterize exposure, including via inhalation and dermal sorption from air.



### INTRODUCTION

Flame retardants (FRs) are often added to textiles and polymers to reduce their flammability. They are most often applied to products that are susceptible to fire and required to meet strict fire safety regulations, such as construction materials, furniture, mattresses, baby products, and electronic items.<sup>1–4</sup> The major classes of commonly used flame retardants include inorganic, halogenated organic, organophosphorus, and nitrogen-based compounds.<sup>4</sup> However, much scientific attention over the past few years has focused on halogenated flame retardants (e.g., brominated and chlorinated).

Polybrominated diphenyl ethers (PBDEs) were the most common flame retardants applied to polyurethane-containing furniture and baby products in the United States before 2005.<sup>1,2</sup> At the end of 2004, U.S. manufacturers agreed to begin to voluntarily phase out PentaBDE and OctaBDE, two common mixtures of PBDEs, because of concerns over their persistence, bioaccumulation, and potential toxicity in both animals and humans.<sup>5–7</sup> Despite this phase out, PentaBDE congeners are still detected with high frequency in human serum in the United States, particularly in children.<sup>8,9</sup> DecaBDE is a third commercial PBDE flame retardant mixture that is commonly applied to electronics (e.g., high-impact polystyrene), with minor applications in textiles, and is also scheduled to be phased out by the end of 2013.<sup>10</sup>

While the home and work environments have attracted a majority of the scientific interest with regard to identifying flame retardant-treated products<sup>1,2</sup> and measuring human exposure,<sup>9,11–13</sup> recreational activities and associated equipment have received little attention.<sup>14</sup> Tents and other camping equipment meet a voluntary U.S. industrial flammability standard known as CPAI-84, which was established by the trade group Canvas Products Association International in response to fire incidents involving tents. The standard requires that tent fabrics pass a vertical flame test with a 12 s ignition time.<sup>15</sup> However, to the best of our knowledge, no information about what types, if any, of flame retardant applications or chemicals are being used to meet CPAI-84 is currently publicly available.

The goals of this study were twofold: (1) to identify and determine if additive flame retardant compounds might currently be applied to camping tents and (2) if flame retardant chemicals are found in tents, to determine whether these chemicals are likely to be transferred to the hands of individuals using the equipment, indicating exposure. The former question

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Table 1. Levels of Flame Retardants Measured in Hand Wipes and Tent Wipes<sup>a</sup>

	hand wipes (ng) (n = 27)			tent wipes (ng) (n = 20)		
	% detected	median	range	% detected	median	range
BDE-47	100	4.1	0.42–40.5	25	NR <sup>d</sup>	<0.11–1.65
BDE-99	100	3.6	0.33–61.7	25	NR <sup>d</sup>	<0.06–0.25
BDE-100	78	0.6	<0.08–8.03	5	NR <sup>d</sup>	<0.02–0.23
BDE-154	41	NR <sup>d</sup>	<0.14–3.44	0	NR <sup>d</sup>	<0.01
BDE-153	48	NR <sup>d</sup>	<0.05–4.14	35	NR <sup>d</sup>	<0.03–3.2
ΣPentaBDE <sup>b</sup>	100	8.48	0.96–117	50	0.39	<0.13–3.2
BDE-209	93	263	<4.9–18300	70	25.3	<4.88–7103
TDCPP	81	710	<34–8530	85	3960	<22–23890
TPP	100	89.7	14.6–362	90	391	<25–4120
TBBPA	ND <sup>c</sup>	NR <sup>d</sup>	N/A	5	NR <sup>d</sup>	<3–13000

<sup>a</sup>Values not normalized to surface area. <sup>b</sup>Represents the sum of BDE-47, BDE-99, BDE-100, BDE-153, and BDE-154. <sup>c</sup>Not detected. <sup>d</sup>Not reported. Medians not calculated when <50% detected.

was examined through the analysis of actual fabric samples from tents; the latter was addressed by analyzing samples of paired tent wipes and hand wipes collected from individuals after they set up their tents. Our group has previously demonstrated that PBDE levels measured in hand wipes are significantly associated with PBDE body burdens, suggesting that hand wipes may be useful predictors of exposure.<sup>9,12</sup> Using these approaches, we hoped to gain more information about flame retardant applications in tents and assess the potential for FR exposure from the handling of treated products.

## MATERIALS AND METHODS

**Collection of Tent Fabrics for Testing.** Eleven different tents were tested for flame retardant applications by cutting out a small piece (approximately 9 cm<sup>2</sup>) for analysis. Samples were collected from colleagues and peers of the authors at Duke University. Small pieces were cut either from the tent wall (if the owner no longer used the tent) or from pockets or ties made of the same material as the tent's main surfaces. For logistical reasons, the tent fabrics destructively tested were not the same tents sampled as part of the tent wipe and hand wipe sampling effort.

**Participants and Field Sampling.** All aspects of this study were authorized by Duke University's Institutional Review Board, and all participants provided informed consent prior to sample collection. Participants setting up tents at a camping site in North Carolina were approached and asked to participate in this study. All sampling occurred over a period of 1 month. Twenty-seven individuals agreed to participate in this study and provide a tent wipe and hand wipe for analysis. Because some of the tents were large, we collected one tent wipe and several hand wipes from all individuals helping to set up the tent. Therefore, for each one tent wipe collected, we collected one to four paired hand wipe samples.

For each participant, we collected a tent wipe, identifying a surface area of 1 ft<sup>2</sup> (929 cm<sup>2</sup>) with a cardboard template on the outer surface of the tent. Tent and hand wipes were collected using a previously established method.<sup>16</sup> For each sample, a sterile gauze pad (7.6 cm × 7.6 cm) was briefly immersed in 3.0 mL of isopropyl alcohol in a clean aluminum weigh boat and immediately used to wipe the area of the exterior fabric surface of the tent, not including the tent fly. The tent wipe was quickly wrapped in clean aluminum foil, placed in a small Ziploc bag, and stored at –20 °C until the wipe could be analyzed.

We collected 27 hand wipe samples from participants associated with 11 different tents immediately after they

constructed them. Sample collections occurred during intermittent rainfall; consequently, several individuals who consented to participate and provided a tent wipe left the area immediately after tent setup and were unavailable for hand wipe collection. Therefore, 20 tent wipe samples were collected, but only 11 of these samples had paired hand wipe samples. Hand wipes were collected by wiping the surface area of the hands from wrist to fingertips, including the backside of the hands, the palms, the fingers, and the area between the fingers. We used one hand wipe for both hands. Each hand wipe was wrapped in clean aluminum foil and placed in a small Ziploc bag and stored at –20 °C until it was analyzed. Participants were also asked to complete a short questionnaire about their tents.

**Sample Extractions and Analysis.** Tent fabric samples were extracted using previously published methods developed for polyurethane foam.<sup>2</sup> Tent wipes and hand wipes were extracted using previously published methods with minor modifications.<sup>9,17</sup> More details about the extraction methods, quantification of analytes, and QA/QC are provided in the Supporting Information.

**Statistical Analysis.** As the levels of flame retardants measured for tents and hand wipes were not normally distributed, we report medians and ranges. Associations between tent wipes and matched hand wipes were examined using nonparametric statistics: Spearman's rank order correlation and Kendall's  $\tau$  (which performs better with tied data). Statistical significance was set at  $\alpha = 0.05$ . Statistical analysis was conducted using R.

## RESULTS AND DISCUSSION

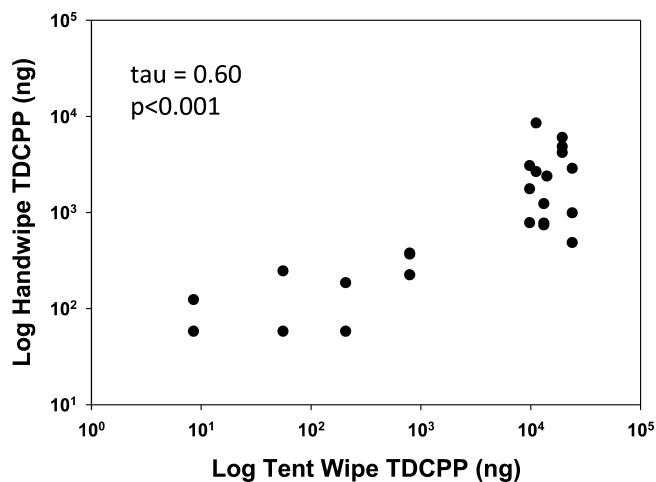
Eleven textile samples were collected from 10 tents and one camping alcove and analyzed for additive flame retardant chemicals. A summary of our findings is presented in Table S1 of the Supporting Information. Decabromodiphenyl ether (BDE-209) was the most common flame retardant, detected in four tent fabric samples at concentrations ranging from 3.92 to 17.8 mg/g. Tris(1,3-dichloroisopropyl) phosphate (TDCPP) was the second most commonly detected flame retardant, positively identified in three of the tents at concentrations of approximately 10 mg/g, or 1% of the fabric mass. Triphenyl phosphate (TPP) was identified in one tent and one alcove at concentrations of 34.6 and 37.5 mg/g, respectively. Tetrabromobisphenol-A (TBBPA) was identified in one tent sample at a concentration of 25.7 mg/g. One tent did not contain any of the flame retardant compounds being tested. These data clearly indicate that additive flame retardants are being applied

to tent fabrics to meet the CPAI-84 flammability standard. Labels indicating that the tent met CPAI-84 requirements were found in six of the 11 tents sampled. No reference to CPAI-84 was found on the remaining tents; however, it is unknown whether such a label might previously have existed on the packaging and/or if the label had been removed. Because of the small sample size, we did not conduct any statistical analyses with year of purchase, country of manufacture, or tent capacity.

As a second line of investigation, we collected samples of tent wipes and hand wipes from adults camping in North Carolina as described above. During analysis of the tent wipe samples, multiple flame retardant chemicals were often detected; however, in all cases, one flame retardant chemical had much higher levels than the other flame retardant(s), suggesting that one flame retardant was intentionally added to the material, while other flame retardants were from background, ubiquitous exposures (e.g., small amounts of PentaBDE congeners). TDCPP was the most common flame retardant detected in the tent wipe samples (Table 1); in 11 of the 20 samples, the mass of TDCPP was more than 1000 ng. BDE-209 was detected in 14 of the tent wipes, from a minimum of 7 ng to a maximum of 7103 ng. TPP was also frequently detected in the tent wipes with a median level of 391 ng. TBBPA was detected in just one tent wipe at a level of 13000 ng. The wide range of flame retardant levels measured among the tent wipe samples and the fact that the same flame retardants were measured at high application rates in tent fabric samples suggest that the tent wipes were detecting flame retardant treatments on the tents.

These same flame retardant chemicals were also frequently detected in participants' hand wipe samples (Table 1). TDCPP and BDE-209 were the most abundant flame retardants detected in the hand wipes. PBDE congeners associated with the PentaBDE commercial mixture (i.e., BDE-47, BDE-99, and BDE-100) were also frequently detected, but at levels much lower than that of BDE-209. In contrast, previous studies measured flame retardant levels on hand wipes collected in home and office environments and found higher levels of the PentaBDE congeners.<sup>9,12</sup> The median TDCPP level was 710 ng in hand wipes, while the median level of BDE-209 was 263 ng, significantly higher than the measured levels of the ubiquitous PentaBDE congeners like BDE-47, which had a median mass of 4.1 ng. To the best of our knowledge, there are no published values for TDCPP or other organophosphate flame retardants in hand wipe samples. Therefore, it is difficult to determine whether these measurements are considerably higher than what would be expected among the general population. However, TDCPP has been ubiquitously detected in house dust, and its metabolite is frequently detected in human urine samples.<sup>13,18</sup> In house dust, TDCPP levels are typically equivalent to or greater than the PBDE levels.

Using these data, correlation analyses were conducted to determine if tent wipe flame retardant levels were significant predictors of levels in paired hand wipes. As seen in Figure 1, the level of TDCPP in a tent wipe was significantly associated with corresponding hand wipe levels ( $\tau = 0.60$ ;  $p < 0.001$ ). Associations were not as strong but still significant for TPP ( $\tau = 0.43$ ;  $p = 0.003$ ) and BDE-209 ( $\tau = 0.37$ ;  $p = 0.01$ ). (Figures S1 and S2 of the Supporting Information). However, these analyses ignore the clustering of the data, potentially underestimating  $p$  values. Applying the Spearman statistic to the average hand wipe level per tent versus tent wipe produced a highly significant result for TDCPP ( $\rho = 0.85$ ;  $p < 0.001$ ) but



**Figure 1.** Association of TDCPP in tent wipes and paired hand wipe samples.

nonsignificant associations for TPP and BDE-209. Hence, we are confident only of the association for TDCPP.

These results suggest that individuals are exposed to flame retardant chemicals following contact with treated textiles. It is not clear whether direct contact with other flame retardant-treated products (e.g., sofas, chairs, TVs, etc.) would also lead to direct partitioning on the skin surface. Dermal absorption of some of these chemicals, particularly BDE-209, may be low. Nevertheless, inadvertent ingestion of these chemicals could occur through hand-to-mouth transfer activities. As noted earlier, previous studies have found significant associations between PBDE levels in hand wipes and PentaBDE levels in serum, suggesting that hand-to-mouth behavior and dermal absorption are significant exposure routes for flame retardants.<sup>9,12</sup> In a study investigating PBDE exposures in U.S. toddlers, PBDE levels on hand wipes were found to be the strongest predictor of serum PBDE levels,<sup>9</sup> highlighting a need to improve our understanding of exposure from hand-to-mouth contact and/or direct dermal absorption. Furthermore, inhalation could be a route of exposure for individuals sleeping inside tents, particularly for organophosphate flame retardants such as TDCPP. The estimated vapor pressure (EpiWin version 4.1) for TDCPP is 4 orders of magnitude higher than the vapor pressure of TBBPA and BDE-209.

Exposures to flame retardants have been associated with health effects, leading to voluntary phase outs by manufacturers for PBDE commercial mixtures and now TDCPP.<sup>19</sup> PBDEs are known endocrine disruptors and have been found to be significantly associated with deficits in motor function, development, and IQ.<sup>6,20,21</sup> TDCPP is considered a probable human carcinogen and is listed on California's Proposition 65 list of carcinogenic and reproductive chemicals.<sup>22</sup> Besides its disruptive roles in immune response and thyroid hormone signaling, TBBPA has recently been shown to mimic estradiol's structure and activate its receptor sites, meaning exposure may lead to excessive estrogen buildup that can increase the risk of cancer.<sup>23</sup> Furthermore, chronic TBBPA exposure has now been shown to induce malignant uterine tumor formation in rats and mice.<sup>24</sup>

Strengths of our study include the measurement of organophosphate flame retardants on hand wipes (not previously reported), the use of product wipes, and the paired sampling of hand wipes and tent wipes. Weaknesses include the



small sample size and convenience sampling. Unfortunately, we were not able to collect paired tent wipes from the tent fabric samples destructively tested in this study. Additional work is needed to demonstrate that product wipes reflect product content. Hand wipes taken before and after handling products<sup>14</sup> would be more conclusive than correlations of levels in demonstrating that tents are the source of exposure. However, it is difficult to see how other sources of exposure could have confounded the observed relationships.

Given these considerations, future studies are needed to evaluate the potential for exposure to additive chemicals in consumer products through direct contact with chemically treated items, particularly those used frequently by children or pregnant women. For example, many of the toy tents and tunnels designed for children to use indoors also meet the flammability requirements of CPAI-84, yet it is unclear whether these products are treated with the same flame retardants that were identified in this study. Given the recent change in the California flammability standard for polyurethane foam in furniture, evaluation of the effectiveness and potential health risks from flame retardants used to meet CPAI-84 appears to be warranted.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

Additional information about the methods used, a table of measured values in the tent fabrics, and figures depicting the associations between TPP and BDE-209 in hand wipes and tent wipes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Author Contributions

A.S.K. and N.P.R. contributed equally to this work.

### Notes

The authors declare no competing financial interest.

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