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Organophosphate flame retardants in dust collected from United States fire stations

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A B S T R A C T

Firefighters are exposed to chemicals during fire events and we previously demonstrated that fire station dust has high levels of polybrominated diphenyl ethers (PBDEs). In conducting the Fire Station Dust Study, we sought to further characterize the chemicals to which firefighters could be exposed – measuring the emerging class of phosphorous-containing flame retardants (PFRs) in fire stations, for the first time, as well as PBDEs. Dust samples from 26 fire stations in five states were collected from vacuum-cleaner bags and analyzed for PFRs and PBDEs. PFR concentrations were found to be on the same order of magnitude as PBDE concentrations (maximum PFR: 218,000 ng/g; maximum PBDE: 351,000 ng/g). Median concentrations of tri-n-butyl phosphate (TNBP), tris (2-chloroisopropyl) phosphate (TCIPP), and tris(1,3-dichloroisopropyl)phosphate (TDCIPP) in dust from fire stations were higher than those previously reported in homes and other occupational settings around the world. Total PFR levels did not vary significantly among states. Levels of TDCIPP were higher in stations where vacuum cleaners were used to clean surfaces other than the floor. PBDE levels were comparable to those found in our previous study of 20 California fire stations and much higher than levels in California residences. PFR and PBDE levels in fire station dust are higher than in other occupational and residential settings, underscoring the need to identify and control sources of this contamination.

1. Introduction

Flame retardants have been used widely in United States consumer products such as furniture foam, plastic electronics casings, and even clothing since the 1970s with the intention of delaying the ignition of fire (U. S. EPA, 2014). Concern over adverse health effects, persistence, and bioaccumulation has led to the phase-out of one class of flame retardants known as polybrominated diphenyl ethers (PBDEs) (U. S. EPA, 2014) and phosphorous-containing flame retardants (PFRs) have emerged as replacements in the commercial market (Dodson et al., 2012; Stapleton et al., 2012). The effects of PFRs on human health have not been well described, though animal research suggests these chemicals may act as endocrine disruptors (Liu et al., 2012; Chen et al., 2015). The chlorinated PFRs tris(chloroethyl)phosphate (TCEP) and tris (1,3-dichloroisopropyl)phosphate (TDCIPP) have been associated with carcinogenicity in animals (van der Veen and de Boer, 2012; CA EPA, 2017a); rats fed TCEP for two years developed kidney tumors and rats fed TDCIPP for two years developed tumors of the kidney, liver, testis, and adrenal gland (Agency for Toxic Substances and Disease Registry, 2012). PFRs have been found in the indoor air(Sjödin et al., 2001; Bradman et al., 2014) and dust(Bradman et al., 2014; Stapleton et al., 2009) of multiple microenvironments (van der Veen and de Boer, 2012), including work environments; however, PFRs have not been previously measured in fire stations.

Firefighters experience a wide range of occupational health hazards, from ergonomic hazards (Walton et al., 2003; Chiou et al., 2012; Plat et al., 2012) to post-traumatic stress (Plat et al., 2012; Berninger et al., 2010; Webber et al., 2011; Fushimi, 2012) to overexertion (Walton et al., 2003). They also may be at increased risk for leukemia (Daniels et al., 2015), testicular cancer (Bates et al., 2001; LeMasters et al., 2006; Bates, 2007), prostate cancer (LeMasters et al., 2006; Bates, 2007), multiple myeloma (LeMasters et al., 2006), and malignant mesothelioma (Daniels et al., 2014). Firefighters are exposed to a wide range of chemicals including flame retardants (Horn et al., 2016; Jayatilaka et al., 2017) while they actively suppress fires (Jankovic et al., 1991; McDiarmid et al., 1991; Fent and Evans, 2011; Laitinen et al., 2012;

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McNamara et al., 2012; Fent et al., 2014; Evans and Fent, 2015) or check for hidden fires after completing fire suppression (Wobst et al., 1999; Bolstad-Johnson et al., 2000; Burgess et al., 2001; Baxter et al., 2014). However, firefighters spend a considerable amount of on-shift downtime at their fire stations, where their exposures to chemicals have not been well characterized.

In 2010–2011, as part of the Firefighter Occupational Exposures (FOX) study, concentrations of PBDEs, novel brominated flame retardants, polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls were measured in dust samples collected from the vacuum cleaner bags of 20 fire stations in Southern California (Shen et al., 2015; Brown et al., 2014). The FOX study found elevated levels of BDE-209, in particular, when compared to other occupational and residential settings. Specifically, the FOX study found that median BDE-209 concentrations were 18-fold higher in dust from fire stations than in dust collected during the same time period from California residences and analyzed by the same methodologies (Shen et al., 2015). This, along with the elevated PBDE concentrations in the blood of FOX participants (Shaw et al., 2013; Park et al., 2015), indicates that California firefighters are exposed to higher levels of certain PBDEs than the general population.

In this follow-up study of 26 additional fire stations from five states, concentrations of PFRs were measured in fire station dust for the first time. The presence of high levels of PBDEs in dust from California homes has been reported in multiple studies (Dodson et al., 2012; Zota et al., 2008), likely as a result of California's unique flammability standards. Correspondingly, this study sought to evaluate whether California fire stations had uniquely high levels of PBDEs or if elevated PBDE levels were also present in fire stations located in other states.

2. Materials and methods

2.1. Fire station recruitment

In 2015, the Fire Station Dust Study (FSDS) worked with the International Association of Fire Fighters (IAFF) to recruit five fire stations from each of five states (California, Minnesota, New Hampshire, New York, Texas). An additional pilot fire station from California was used to refine sampling protocols prior to launching the study.

2.2. Dust sampling

We collected bags from vacuum cleaners used for routine dust removal in the living quarters of 26 fire stations in 2015. We mailed sampling packets to each fire station and included: 1) a sampling protocol describing how to seal and ship the vacuum bag; 2) a re-sealable 36 cm × 61 cm × 0.2-mm thick polyethylene bag to contain the vacuum cleaner bag; 3) a questionnaire acquiring general fire station information and fire station cleaning practices; and 4) a preaddressed, prepaid envelope in which to mail the vacuum-cleaner bag to the Environmental Chemistry Laboratory at the California Department of Toxic Substances Control (DTSC) in Berkeley, California. We received a total of 26 vacuum-cleaner bags, including the vacuum-cleaner bag from the pilot fire station. Samples remained in the polyethylene bag at room temperature at DTSC until analysis.

2.3. Surveys

Fire station personnel completed a survey about the brand and model of their vacuum cleaner as well as the cleaning protocols they use for fire engines, fire stations, and turnout gear in an attempt to capture potential determinants of flame retardant concentrations.

2.4. Chemical analysis

Dust samples were sieved to remove fibers and debris larger than 150 μm. The extraction method was adapted from a previously described method (Van den Eede et al., 2012). Briefly, we weighed approximately 50 mg of the resulting fine-dust fraction, spiked it with a mixture of labeled internal standards (Supporting Information, Table S1) and extracted the analytes by sonication in a 3:1 hexane:acetone solution. The extracts were cleaned using Florisil column chromatography, then solvent-exchanged into isooctane and spiked with two labeled injection standards (Supporting Information, Table S1) yielding final extract volumes of 100 μL for the PBDE fraction and 1 mL for the PFR fraction. We analyzed the samples in three sample batches: the first two batches contained nine dust samples and the third batch contained eight dust samples. Each sample batch also contained a duplicate, two method blanks, a laboratory control, and a standard reference material (NIST SRM No. 2585; Supporting Information, Table S2). We analyzed the extracts for five PFRs using electron impact ionization mode gas chromatography-tandem mass spectrometry (CA EPA, 2017b). We also analyzed 18 PBDEs via high-resolution gas chromatography–mass spectrometry operated in electron impact ionization mode, following the same analytical protocols we described in the FOX study for dust samples collected from Southern California fire stations (Shen et al., 2015) and reference California homes (Whitehead et al., 2013). We calculated method reporting limits (MRLs) as three times the standard deviation of the method blank values for each analyte from three sample batches.

2.5. Statistical methods

Summary statistics and figures were generated using Microsoft Excel (Microsoft Office 2011 for Mac OS X). Statistical analyses were performed in R (R Core Team. 2016. *R: A language and environment for statistical computing*. Vienna, Austria: R Foundation for Statistical Computing). Pearson correlation coefficients were used to evaluate the relationships between analytes. To characterize the geographic variability of the flame retardants, we estimated within-state (σ_w^2) and between-state (σ_b^2) variance components and then calculated two descriptive ratios using the following equations:

$$\text{Lambda, } \lambda = \frac{\sigma^2{}_w}{\sigma^2{}_b} \tag{1}$$

$$\text{Intraclass correlation coefficient, } \rho = \frac{\sigma^2{}_b}{\sigma^2{}_b + \sigma^2{}_w} \tag{2}$$

We tested for differences in flame retardant levels by other explanatory factors (including age of building, turnout gear cleaning policies, turnout gear storage policies, and vacuum cleaner usage) using ANOVA. Chemical concentrations were log transformed prior to analysis. Significant associations were determined at $\alpha \leq 0.05$.

3. Results and discussion

3.1. Characteristics of fire stations

A survey was returned by 25 of the 26 fire stations (6 of 6 from California, 5 of 5 from Minnesota, 5 of 5 from New Hampshire, 5 of 5 from New York, 4 of 5 from Texas). About half (56%) of the fire stations were built before 1970 and the rest (44%) were built after 1970. Most of the fire stations had turnout gear cleaning policies (80%) and designated areas for turnout gear storage (92%). In 68% of fire stations turnout gear was stored in the apparatus bay, in 4% in the living quarters, and in 12% in another space (16% of fire stations did not respond to this question). Turnout gear was stored in an enclosed area in 65% of the fire stations, but only 45% of the fire stations had ventilated storage areas. Turnout gear was explicitly banned from 92% of

Table 1
Summary of PFR and PBDE concentrations (ng/g) in 26 dust samples from 26 fire stations in the Fire Station Dust Study (FSDS) [2015], compared to median concentrations in dust samples collected from FOX fire stations [2010–2011; $n = 27$] (Shen et al., 2015) and California residences [2010; $n = 203$] that were analyzed using the same protocols as FSDS samples (Whitehead et al., 2013).

Flame retardant	Method reporting limit (MRL)	% of FSDS samples above MRL	FSDS minimum	FSDS median	FSDS mean	FSDS maximum	FOX median	CA residential median
PFRs								
TNBP	0	100	177	260	358	1480	NM	NM
TCEP	0	100	178	1040	1320	4660	NM	NM
TCIPP	323	100	499	3880	5040	37,400	NM	NM
TDCIPP	1240	100	1650	10,900	22,600	218,000	NM	NM
TPHP	0	100	1150	10,800	14,100	85,400	NM	NM
PBDEs								
BDE-17	0.21	100	1.30	6.87	18.3	195	NM	NM
BDE-28	0.14	100	5.11	24.1	77.4	1000	40.3	20
BDE-47	0.64	100	404	3050	12,800	161,000	5170	1300
BDE-66	0.04	100	9.29	59.9	263	3670	NM	NM
BDE-99	2.07	100	465	4180	22,800	338,000	9240	2100
BDE-100	0.76	100	87.9	756	5000	82,000	1720	330
BDE-153	0.32	100	73.0	489	2300	29,400	1220	290
BDE-154	0.42	100	42.9	344	1730	22,400	919	150
BDE-183	0.12	100	9.05	41.6	113	764	77.9	17
BDE-196	0.03	100	9.06	53.3	62.0	176	76.6	8.2
BDE-197	0.08	100	5.17	25.9	39.3	391	51.1	7.6
BDE-201	0.11	100	4.02	14.3	17.9	41.5	NM	NM
BDE-202	0.05	100	1.22	4.25	5.38	13.7	NM	NM
BDE-203	0.03	100	5.95	61.1	78.8	271	NM	NM
BDE-206	1.24	100	60.1	1900	2340	9490	1130	75
BDE-207	1.84	100	82.6	1130	1230	3320	592	54
BDE-208	0.83	100	51.7	533	578	1400	379	33
BDE-209	73.9	100	1990	57,000	83,300	351,000	47,000	2500

NM = not measured

the fire stations' living quarters.

3.2. Concentrations of flame retardants in dust collected from FSDS fire stations

We detected each of the five PFR compounds in each of the dust samples with concentrations ranging from 177 ng/g to 218,000 ng/g (Table 1; Supporting Information, Table S3).

The highest measured PFRs were on the same order of magnitude as the highest measured PBDEs (maximum PFR, TDCIPP: 218,000 ng/g; maximum PBDE, BDE-209: 351,000 ng/g). TDCIPP and TPHP were the dominant PFR compounds in the dust samples; TDCIPP represented at least 50% of Σ_5PFRs for eight dust samples and TPHP represented at least 50% of Σ_5PFRs for six dust samples (Supporting Information, Fig. S1). TDCIPP was the highest measured PFR in 15 of 26 samples, TPHP was the highest measured PFR in 10 dust samples, and TCIPP was the highest measured PFR in one fire station.

We detected each of the 18 PBDE congeners in each of the dust samples with concentrations ranging from 1.22 ng/g to 351,000 ng/g (Table 1; Supporting Information, Table S3). BDE-209 was the dominant congener found in most of the dust samples followed by BDE-47 and BDE-99; for 21 dust samples, BDE-209 concentrations represented at least 50% of Σ_{18}PBDEs (Supporting Information, Fig. S2).

3.3. Differences in chemical levels within and between states

None of the PFR compounds measured had statistically significant differences among states (Table 2). For some of the flame retardants, the within-state variance estimate was very large making it impossible to observe potential between-state variance; the between-state variance estimate was zero in these instances (Fig. 1).

Dust from Texas had the highest concentrations of TDCIPP and TPHP, but also had the largest within-state variability for both PFRs (Fig. 1, Supporting Information Table S4). Large within-state variance in PFR concentrations made it difficult to assess differences among

Table 2
Estimated variance components and variance ratios from random effects model describing within-state and between-state variability.

Flame retardant	Variance components		Variance ratios	
	Between state, σ_b^2	Within state, σ_w^2	Lambda[a], λ	Intraclass correlation coefficient[b], ρ
PFRs				
TNBP	0	0.20	–	0
TCEP	0	0.62	–	0
TCIPP	0	0.69	–	0
TDCIPP	0.22	1.08	4.92	0.17
TPHP	0	0.83	–	0
PBDEs				
BDE-17	0.16	1.21	7.37	0.12
BDE-28	0.09	1.38	16.19	0.06
BDE-47	0.48	1.61	3.33	0.23
BDE-66	0.31	1.72	5.51	0.15
BDE-99	0.55	1.72	3.13	0.24
BDE-100	0.53	1.78	3.36	0.23
BDE-153	0.42	1.61	3.79	0.21
BDE-154	0.50	1.68	3.35	0.23
BDE-183	0	1.37	–	0
BDE-196*	0.27	0.50	1.84	0.35
BDE-197	0.09	0.77	8.31	0.11
BDE-201*	0.28	0.30	1.08	0.48
BDE-202*	0.35	0.25	0.71	0.59
BDE-203*	0.38	0.86	2.28	0.30
BDE-206*	0.82	1.04	1.27	0.44
BDE-207*	0.42	0.61	1.44	0.41
BDE-208*	0.35	0.46	1.29	0.44
BDE-209*	0.89	1.22	1.36	0.42

* Significance found at $p < 0.05$; null hypothesis: chemical concentrations do not vary among states.
[a] Lambda, $\lambda = \frac{\sigma^2{}_w}{\sigma^2{}_b}$.
[b] Intraclass correlation coefficient, $\rho = \frac{\sigma^2{}_b}{\sigma^2{}_b + \sigma^2{}_w}$

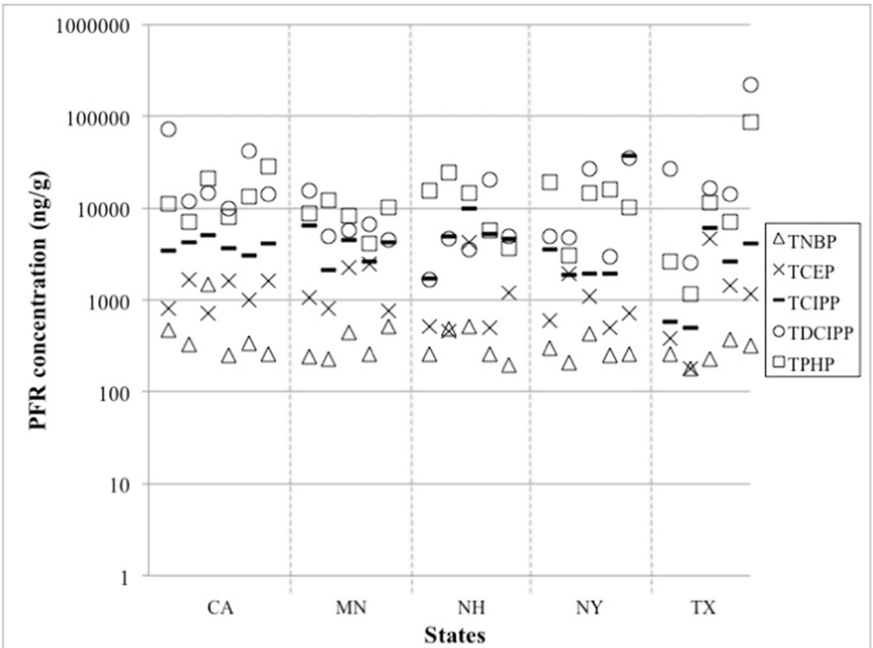

Fig. 1. Concentrations (ng/g) of PFR compounds from each dust sample (n = 26), clustered by state.

states – with intra-class correlation coefficients (ICCs) of no > 0.17 (TDCIPP, Table 2). Future studies with larger sample sizes and information on additional characteristics of fire station activities are required to further elucidate potential differences in PFR levels among the states.

PBDE concentrations also varied widely from different fire stations in the same state. Texas had the largest within-state variability for BDE-47 and BDE-99, and Minnesota had the largest within-state variability for BDE-209 (Fig. 2, Table S4). When compared among states, concentrations of the major BDE congeners (BDE-47, -99, and -209) varied widely. Between-state variance accounted for 23% to 42% of total variance in levels of BDE-47, BDE-99, and BDE-209 (ICC range: 0.23 to 0.42, Table 2). Median levels for the higher brominated BDE congeners were significantly higher in California than in the other four states in the study (BDE-196, p = 0.02; BDE-201, p = 0.003; BDE-202, p = 0.0003; BDE-203, p = 0.03; BDE-206, p = 0.005; BDE-207, p = 0.008; BDE-208, p = 0.005; BDE-209, p = 0.007). Previous studies have reported elevated levels of the *lower* brominated BDEs in California house dust compared to other states. Lower-brominated BDEs are the primary constituents of PentaBDE, the commercial mixture that was used to treat furniture foam in order to achieve compliance with the State's unique furniture flammability standards (Zota et al., 2008). In contrast, *higher* brominated BDEs are not typically found at exceptionally high levels in California house dust when compared to house dust levels from other states (Dodson et al., 2012; Whitehead et al., 2011). These higher-brominated BDEs comprised the other two commercial BDE mixtures, OctaBDE and DecaBDE, which were commonly used in electronics and plastic products (Alaee et al., 2003). In our study, whereas we did not find a significant difference in the *lower* brominated BDEs between the five states; we did observe elevated

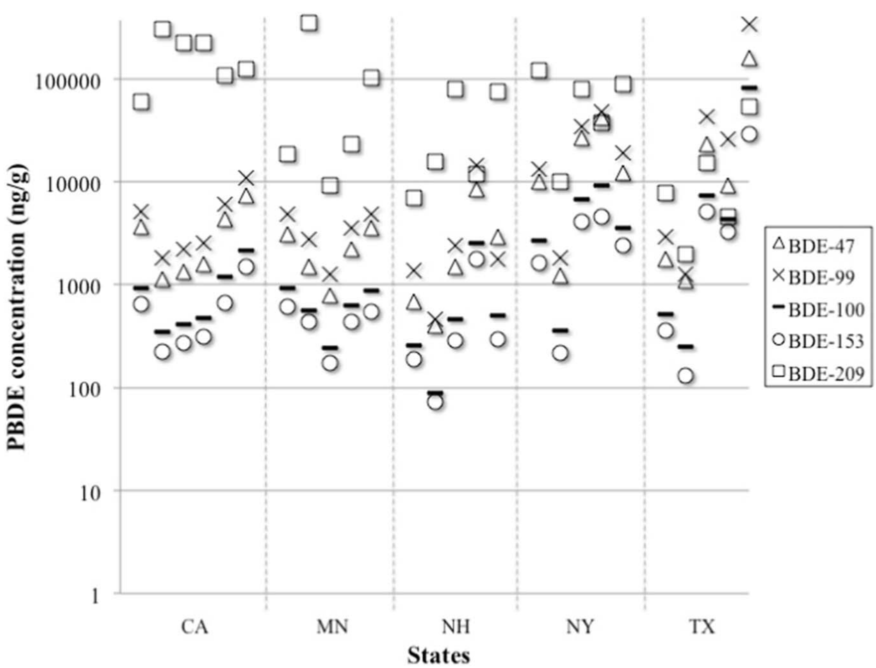

Fig. 2. Concentrations (ng/g) of major PBDE congeners -47, -99, -100, -153, and -209 from each dust sample (n = 26), clustered by state.

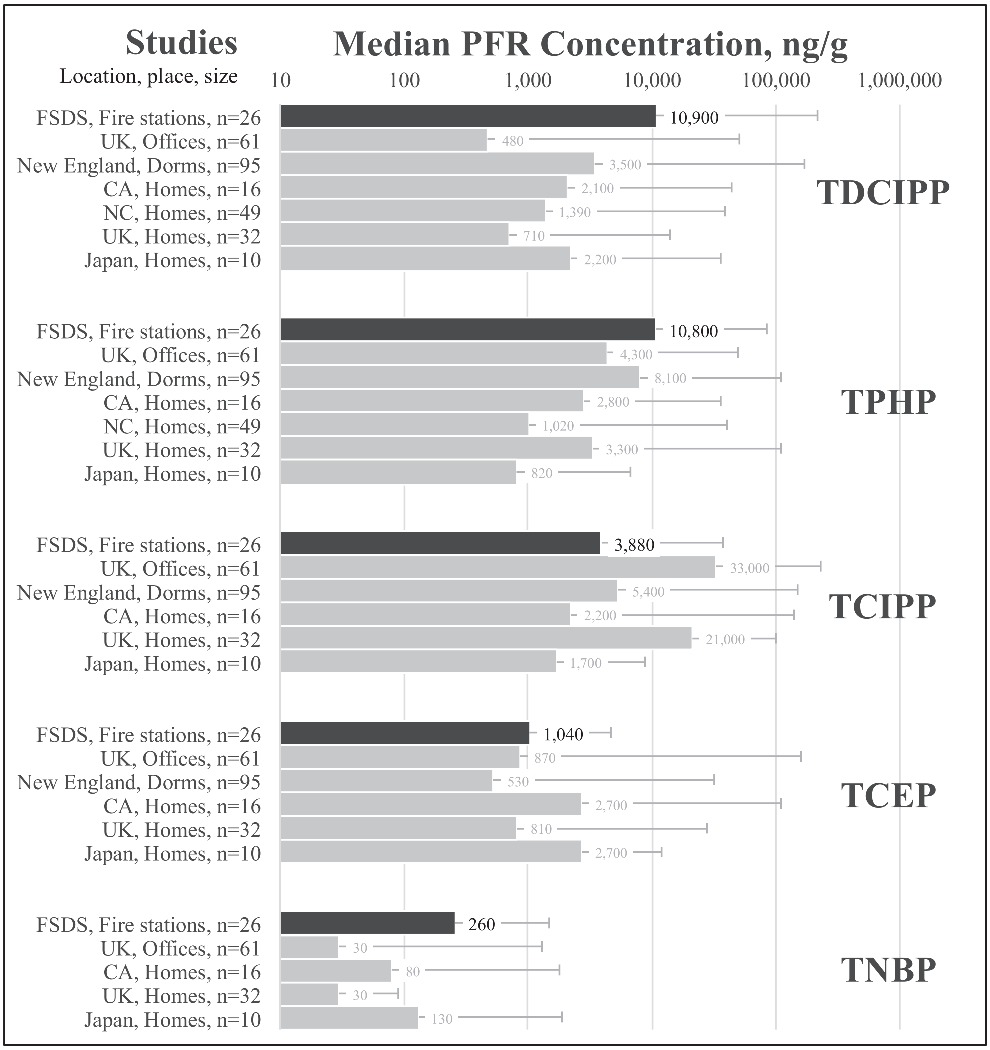

Fig. 3. Median concentrations of PFRs in dust (ng/g, shown on a logarithmic scale) with positive error bars representing maxima from the Fire Station Dust Study (collected in 2015), other occupational settings, and residential settings. Data for UK offices and homes (collected 2011–2012) from Brommer and Harrad (Brommer and Harrad, 2015), for New England dorms (collected in 2015) from Dodson et al. (Dodson et al., 2017) for CA homes (collected in 2011) from Dodson et al. (Dodson et al., 2012) for NC homes (collected in 2012, geometric mean, only TDCIPP and TPHP reported) from Hoffman et al. (Hoffman et al., 2015) and for Japanese homes (collected 2009–2010) from Mizouchi et al.(Mizouchi et al., 2015).

levels of the *higher* brominated BDEs in California. These findings suggest that California fire stations may have a source of elevated PBDE levels that are not associated with the State's unique furniture flammability standard, and that this contamination is perhaps originating from electronics.

3.4. Differences in chemical levels by other explanatory factors

In ANOVA analysis comparing chemical concentrations by vacuum use, where the null hypothesis was that chemical concentrations do not vary by vacuum use, TDCIPP was the only chemical measured to show a significant difference ($p = 0.03$) in levels between fire stations that used vacuum cleaners on floor surfaces only (median TDCIPP: 5800 ng/g) and fire stations that used vacuum cleaners on surfaces other than the floor (median TDCIPP: 27,800 ng/g). TDCIPP and TCEP are both commonly used as flame retardants in textiles (Dodson et al., 2012), though we did not observe a corresponding significant differences in TCEP levels by cleaning practices. There were no significant relationships between flame retardant concentrations and any other explanatory factors.

3.5. Correlation between analytes

Levels of the two dominant PFRs - TDCIPP and TPHP - were not significantly correlated, suggesting that they may originate from different sources. Indeed, though both are used in polyurethane foams, TPHP is also used as a flame retardant plasticizer and as a lubricant (Van den Eede et al., 2011). Additionally, among the PFRs measured in this study, only TPHP is a major component of Firemaster 550, a flame retardant mixture used in furniture foam as a replacement for the phased-out PentaBDE mixture (Stapleton et al., 2008). Within the PFR analytes, only TNBP (used as a plasticizer and lubricant) and TCIPP (used in polyurethane foam) showed significant correlations ($r = 0.43$) with TPHP (used as plasticizer and lubricant, and in polyurethane foam); TCEP and TCIPP (both used in polyurethane foams) were also significantly correlated ($r = 0.43$). TCIPP was also significantly correlated with the higher brominated PBDEs (r range: 0.39–0.44). TDCIPP showed significant correlations with the lower brominated PBDEs (r range: 0.42–0.59); both TDCIPP and lower brominated BDEs that make up PentaBDE are used in polyurethane foams. TPHP had significant correlations with all the brominated flame retardants, excepting BDE-197 (Supporting Information, Table S5). BDE congeners were highly correlated within two groups; Pearson correlation coefficients ranged from 0.66 to 0.99 among the lower brominated PBDEs (BDE-17 to BDE-183), and from 0.71 to 0.99 among the higher brominated PBDEs (BDE-196 to BDE-209).

3.6. Calculating exposure doses

This study observed elevated levels of PFRs and PBDEs in fire stations. If one assumes that an 80 kg person ingests 30 mg of dust a day (EPA, 2011), then the maximum PBDE concentrations found in our study – 338,00 ng/g for BDE-99 and 351,000 ng/g for BDE-209 – correspond to doses of 1.27×10^{-4} mg/kg-day for BDE-99 and 1.32×10^{-4} mg/kg-day for BDE-209. The United States Environmental Protection Agency (U.S. EPA) suggests a maximum oral reference dose of 1×10^{-4} mg/kg-day for BDE-99 and 7×10^{-3} mg/kg-day for BDE-209 (the U.S. EPA does not provide oral reference doses for PFRs) (EPA, 2008). Via the unintentional ingestion of settled dust, firefighters at certain fire stations may be exposed to levels of BDE-99 over the U.S. EPA's suggested levels. Firefighter *total* exposure doses could be even higher if all routes of exposure (dermal, diet, inhalation) were considered. Moreover, the previous FOX study observed elevated PBDE levels in firefighter serum compared to a reference population in California (Park et al., 2015), suggesting biological uptake within this occupation.

3.7. Concentrations in fire stations vs. other settings

Median TNBP, TDCIPP, and TPHP levels in fire station dust were higher than those previously reported in occupational and residential settings, including a study that measured PFRs in 2011 in California house dust (Fig. 3) (Dodson et al., 2012).

We also corroborated our findings from the FOX study, showing again that median dust concentrations of all BDE congeners were substantially higher in the FSDS California fire stations than in the reference population of California homes (sampled in 2010, and analyzed using the same analytical protocols). Specifically, the very high levels of BDE-209 observed in dust from California fire stations in the FOX study were once again evident in the California fire stations of the FSDS study (Supporting Information, Fig. S3). In measuring dust-PBDE levels in fire stations from other states for the first time, we found median concentrations of the major BDE congeners to be higher than other occupational settings and residential settings, including in the reference population of California homes (Supporting Information, Fig. S3). Overall, median concentrations of the major BDE congeners were higher in this study than those from other occupational and residential settings; only our previous FOX study has reported higher median concentrations of BDEs-47, -99, -100, and -153 in indoor dust.

Given that fire stations have higher levels of PFRs and PBDEs compared to other occupational and residential settings, future research should focus on implicating flame retardant sources that are unique to fire stations such as specialized firefighting equipment (e.g., turnout gear and fire engines), and contamination that is tracked back from fire-incident sites. Indeed, some studies have observed contamination of turnout gear surfaces by PFRs (Horn et al., 2016) and PBDEs (Horn et al., 2016; Alexander and Baxter, 2016; Easter et al., 2016) after fire incidents, and some station gear has been shown to purposely contain the mineral flame retardant, antimony (de Perio et al., 2010). These and other studies have demonstrated the potential for dermal absorption of flame retardants by firefighters and the benefit of turnout gear cleaning for reducing PBDE serum levels (Park et al., 2015). As such, we propose that flame retardants may be tracked from fire responses back to fire stations via contaminated turnout gear, resulting in the contamination of fire station dust. Chemical track-back such as this has been observed in agricultural communities with pesticides (Curl et al., 2002; Coronado et al., 2006; Suarez-Lopez et al., 2012). Moreover, the previous FOX study found a positive relationship between PAH levels in fire station dust and the number of fire and hazardous material incidents, suggesting that firefighters track-back PAHs on contaminated gear and equipment from fire incidents to the fire station (Shen et al., 2015). Although we were unable to obtain information regarding the number of responses to fire incidents per station for this study, future studies should include this information along with turnout gear wipe and fire station dust measurements to further elucidate potential track-back of flame retardants from fire sites to fire stations. Future studies should also include analyses examining the relationship between flame retardant levels in dust and consumer products, such as furniture and electronics, which are present in the fire stations. The quantities of specific consumer products within a household have been shown to be positively correlated with PBDE levels in house dust (e.g., furniture associated with PentaBDE and electronics associated with DecaBDE) (Allen et al., 2008). Given that consumer products are often the source of flame retardant contamination in residential homes (U. S. EPA, 2014; Zota et al., 2008; Allen et al., 2008), the amount of consumer products in fire stations such as beds, couches, recliners, televisions, and computers could potentially explain the differences in flame retardant levels between fire stations and residential homes. Future research should include detailed surveys observing the types and number of consumer products, and amount of foot traffic within fire stations to compare to households for evaluation of flame retardant level differences. Additionally, information on the type of flammability standard that furniture in each fire station follows (e.g., TB117-2013; TB133; or other) may elucidate observed differences (Dodson et al., 2017). Such research would inform intervention practices to reduce flame retardant levels in fire stations and potentially reduce the exposure to flame retardants experienced by firefighters.

3.8. Limitations

We sampled dust collected from vacuum cleaners used for everyday cleaning at each fire station. The main advantages to this method are integration of chemical levels over space and time, convenience, and cost efficiency. The main limitation to this method is that vacuum cleaners and vacuum cleaning practices may differ from one fire station to the next, and introduce variability in chemical levels. Furthermore, we could not eliminate the possibility that the vacuum cleaners were made of materials containing either PFRs or PBDEs, potentially causing us to overestimate PFR and PBDE levels in the fire station dust. However, the vacuum cleaners were commercially-available residential models which are commonly used in California homes (Whitehead et al., 2013), one of the comparison populations used in this analysis. In spite of its limitations, vacuum-bag dust remains a useful medium for measuring indoor chemical contamination because indoor dust acts as a reservoir for semivolatile and nonvolatile environmental contaminants.

Despite a limited number of samples, we were able to observe statistically significant differences in PBDE concentrations among states. Specifically, BDEs 196, 201, 202, 203, 206, 207, 208, and 209 were higher in California fire stations than in fire stations from the other four states. For future studies, a larger sample size may assist in more rigorous statistical analyses to identify potential differences among states in PFR levels and explain differences in PBDE levels by state more conclusively.

4. Conclusions

Our findings from this study, as well as the previous FOX study, indicate that fire stations are contaminated with higher levels of flame retardants than residences and other occupational settings; thus, firefighters may be potentially exposed to higher levels of flame retardants than the general population. This follow-up study confirmed that flame retardant levels were elevated in fire stations from multiple states in addition to California. Future studies should focus on identifying the sources of flame retardants that are unique to fire stations such as contaminated gear and equipment, chemical track-back from fire incidents, or specific types of furnishings.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envint.2017.12.009.

References

Agency for Toxic Substances and Disease Registry, 2012. United States Department of Health and Human Services. Toxicological Profile for Phosphate Ester Flame Retardants.

Alaee, M., Arias, P., Sjödin, A., Bergman, A., 2003. An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release. Environ. Int. 29 (6), 683–689.

Alexander, B.M., Baxter, C.S., 2016. Flame-retardant contamination of firefighter personal protective clothing – a potential health risk for firefighters. J. Occup. Environ. Hyg. 13 (9), D148–D155.

Allen, J.G., McClean, M.D., Stapleton, H.M., Webster, T.F., 2008. Linking PBDEs in house dust to consumer products using X-ray fluorescence. Environ. Sci. Technol. 42 (11), 4222–4228.

Bates, M.N., 2007. Registry-based case–control study of cancer in California firefighters. Am. J. Ind. Med. 50 (5), 339–344.

Bates, M.N., Fawcett, J., Garrett, N., Arnold, R., Pearce, N., Woodward, A., 2001. Is testicular cancer an occupational disease of fire fighters? Am. J. Ind. Med. 40 (3), 263–270.

Baxter, C.S., Hoffman, J.D., Knipp, M.J., Reponen, T., Haynes, E.N., 2014. Exposure of firefighters to particulates and polycyclic aromatic hydrocarbons. J. Occup. Environ. Hyg. 11 (7), D85–D91.

Berninger, A., Webber, M.P., Niles, J.K., Gustave, J., Lee, R., Cohen, H.W., Kelly, K., Corrigan, M., Prezant, D.J., 2010. Longitudinal study of probable post-traumatic stress disorder in firefighters exposed to the world trade center disaster. Am. J. Ind. Med. 53 (12), 1177–1185.

Bolstad-Johnson, D.M., Burgess, J.L., Crutchfield, C.D., Storment, S., Gerkin, R., Wilson, J.R., 2000. Characterization of firefighter exposures during fire overhaul. AIHAJ. 61 (5), 636–641.

Bradman, A., Castorina, R., Gaspar, F., Nishioka, M., Colón, M., Weathers, W., Egeghy, P.P., Maddalena, R., Williams, J., Jenkins, P.L., McKone, T.E., 2014. Flame retardant exposures in California early childhood education environments. Chemosphere 116, 61–66.

Brommer, S., Harrad, S., 2015. Sources and human exposure implications of concentrations of organophosphate flame retardants in dust from UK cars, classrooms, living rooms, and offices. Environ. Int. 83, 202–207.

Brown, F.R., Whitehead, T.P., Park, J.S., Metayer, C., Petreas, M.X., 2014. Levels of non-polybrominated diphenyl ether brominated flame retardants in residential house dust samples and fire station dust samples in California. Environ. Res. 135, 9–14.

Burgess, J.L., Nanson, C.J., Bolstad-Johnson, D.M., Gerkin, R., Hysong, T.A., Lantz, R.C., Sherrill, D.L., Crutchfield, C.D., Quan, S.F., Bernard, A.M., Witten, M.L., 2001. Adverse respiratory effects following overhaul in firefighters. J. Occup. Environ. Med. 43 (5), 467–473.

CA EPA, 2017a. Chemicals known to the state to cause cancer or reproductive toxicity. California Environmental Protection Agency, Office of Environmental Health Hazard Assessment, Sacramento, CA.

CA EPA, 2017b. Standard Operating Procedure - Determination of Organophosphate and Brominated Flame Retardants in House Dust and Consumer Products by Gas Chromatography-Tandem Mass Spectrometry. Department of Toxic Substances Control, Berkeley, CA DCN: 05.0029.00.

Chen, G., Jin, Y., Wu, Y., Liu, L., Fu, Z., 2015. Exposure of male mice to two kinds of organophosphate flame retardants (OPFRs) induced oxidative stress and endocrine disruption. Environ. Toxicol. Pharmacol. 40 (1), 310–318.

Chiou, S.S., Turner, N., Zwiener, J., Weaver, D.L., Haskell, W.E., 2012. Effect of boot weight and sole flexibility on gait and physiological responses of firefighters in stepping over obstacles. Hum. Factors 54 (3), 373–386.

Coronado, G.D., Vigoren, E.M., Thompson, B., Griffith, W.C., Faustman, E.M., 2006. Organophosphate pesticide exposure and work in pome fruit: evidence for the take-home pesticide pathway. Environ. Health Perspect. 114 (7), 999–1006.

Curl, C.L., Fenske, R.A., Kissel, J.C., Shirai, J.H., Moate, T.F., Griffith, W., Coronado, G., Thompson, B., 2002. Evaluation of take-home organophosphorus pesticide exposure among agricultural workers and their children. Environ. Health Perspect. 110 (12), A787–A792.

Daniels, R.D., Kubale, T.L., Yiin, J.H., Dahm, M.M., Hales, T.R., Baris, D., Zahm, S.H., Beaumont, J.J., Waters, K.M., Pinkerton, L.E., 2014. Mortality and cancer incidence in a pooled cohort of US firefighters from San Francisco, Chicago and Philadelphia (1950–2009). Occup. Environ. Med. 71 (6), 388–397.

Daniels, R.D., Bertke, S., Dahm, M.M., Yiin, J.H., Kubale, T.L., Hales, T.R., Baris, D., Zahm, S.H., Beaumont, J.J., Waters, K.M., Pinkerton, L.E., 2015. Exposure–response relationships for select cancer and non-cancer health outcomes in a cohort of US firefighters from San Francisco, Chicago and Philadelphia (1950–2009). Occup. Environ. Med. 72 (10), 699–706.

Dodson, R.E., Perovich, L.J., Covaci, A., Van den Eede, N., Ionas, A.C., Dirtu, A.C., Brody, J.G., Rudel, R.A., 2012. After the PBDE phase-out: a broad suite of flame retardants in repeat house dust samples from California. Environ. Sci. Technol. 46 (24), 13056–13066.

Dodson, R.E., Rodgers, K.M., Carey, G., Cedeno Laurent, J.G., Covaci, A., Poma, G., Malarvannan, G., Spengler, J.D., Rudel, R.A., Allen, J.G., 2017. Flame retardant chemicals in college dormitories: flammability standards influence dust concentrations. Environ. Sci. Technol. 51 (9), 4860–4869.

Easter, E., Lander, D., Huston, T., 2016. Risk assessment of soils identified on firefighter turnout gear. J. Occup. Environ. Hyg. 13 (9), 647–657.

EPA, U.S., 2008. 2,2′,3,3′,4,4′,5,5′,6,6′-Decabromodiphenyl ether (BDE-209); CASRN 1163-19-5 chemical assessment summary. In: Integrated Risk Information System (IRIS). U. S. Environmental Protection Agency, Washington, DC.

EPA, U.S., 2011. Exposure Factors Handbook 2011 Edition (Final). U. S. Environmental Protection Agency, Washington, DC EPA/600/R-09/052F.

Evans, D.E., Fent, K.W., 2015. Ultrafine and respirable particle exposure during vehicle fire suppression. Environ. Sci. Process. Impacts. 17 (10), 1749–1759.

Fent, K.W., Evans, D.E., 2011. Assessing the risk to firefighters from chemical vapors and gases during vehicle fire suppression. J. Environ. Monit. 13 (3), 536–543.

Fent, K.W., Eisenberg, J., Snawder, J., Sammons, D., Pleil, J.D., Stiegel, M.A., Mueller, C., Horn, G.P., Dalton, J., 2014. Systemic exposure to PAHs and benzene in firefighters suppressing controlled structure fires. Ann. Occup. Hyg. 58 (7), 830–845.

Fushimi, M., 2012. Posttraumatic stress in professional firefighters in Japan: rescue efforts after the great East Japan earthquake (Higashi Nihon Dai-Shinsai). Prehosp. Disaster Med. 27 (5), 416–418.

Hoffman, K., Garantziotis, S., Birnbaum, L.S., Stapleton, H.M., 2015. Monitoring indoor exposure to organophosphate flame retardants: hand wipes and house dust. Environ. Health Perspect. 123 (2), 160–165.

Horn, G., Kerber, S., Fent, K., Fernhall, B., Smith, D., 2016. Cardiovascular & Chemical Exposure Risks in Modern Firefighting. Illinois Fire Service Institute Interim Report.

Jankovic, J., Jones, W., Burkhart, J., Noonan, G., 1991. Environmental study of firefighters. Ann Occup Hyg. 35 (6), 581–602.

Jayatilaka, N.K., Restrepo, P., Williams, L., Ospina, M., Valentin-Blasini, L., Calafat, A.M., 2017. Quantification of three chlorinated dialkyl phosphates, diphenyl phosphate, 2,3,4,5-tetrabromobenzoic acid, and four other organophosphates in human urine by solid phase extraction-high performance liquid chromatography-tandem mass spectrometry. Anal. Bioanal. Chem. 409 (5), 1323–1332.

Laitinen, J., Mäkelä, M., Mikkola, J., Huttu, I., 2012. Firefighters' multiple exposure assessments in practice. Toxicol. Lett. 213 (1), 129–133.

LeMasters, G.K., Genaidy, A.M., Succop, P., Deddens, J., Sobeih, T., Barriera-Viruet, H., Dunning, K., Lockey, J., 2006. Cancer risk among firefighters: a review and meta-analysis of 32 studies. J. Occup. Environ. Med. 48 (11), 1189–1202.

Liu, X., Ji, K., Choi, K., 2012. Endocrine disruption potentials of organophosphate flame retardants and related mechanisms in H295R and MVLN cell lines and in zebrafish. Aquat. Toxicol. 114-115, 173–181.

McDiarmid, M.A., Lees, P.S., Agnew, J., Midzenski, M., Duffy, R., 1991. Reproductive hazards of fire fighting. II. Chemical hazards. Am. J. Ind. Med. 19 (4), 447–472.

McNamara, M.L., Semmens, E.O., Gaskill, S., Palmer, C., Noonan, C.W., Ward, T.J., 2012. Base camp personnel exposure to particulate matter during wildland fire suppression activities. J. Occup. Environ. Hyg. 9 (3), 149–156.

Mizouchi, S., Ichiba, M., Takigami, H., Kajiwara, N., Takamuku, T., Miyajima, T., Kodama, H., Someya, T., Ueno, D., 2015. Exposure assessment of organophosphorus and organobromine flame retardants via indoor dust from elementary schools and domestic houses. Chemosphere 123, 17–25.

Park, J.S., Voss, R.W., McNeel, S., Wu, N., Tan, G., Wang, Y., Israel, L., Das, R., Petreas, M., 2015. High exposure of California firefighters to polybrominated diphenyl ethers. Environ. Sci. Technol. 49 (5), 2948–2958.

de Perio, M.A., Durgam, S., Caldwell, K.L., Eisenberg, J., 2010. A health hazard evaluation of antimony exposure in fire fighters. J. Occup. Environ. Med. 52 (1), 81–84.

Plat, M.C., Frings-Dresen, M.H., Sluiter, J.K., 2012. Diminished health status in firefighters. Ergonomics 55 (9), 1119–1122.

Shaw, S.D., Berger, M.L., Harris, J.H., Yun, S.H., Wu, Q., Liao, C., Blum, A., Stefani, A., Kannan, K., 2013. Persistent organic pollutants including polychlorinated and polybrominated dibenzo-p-dioxins and dibenzofurans in firefighters from northern California. Chemosphere 91 (10), 1386–1394.

Shen, B., Whitehead, T.P., McNeel, S., Brown, F.R., Dhaliwal, J., Das, R., Israel, L., Park, J.S., Petreas, M., 2015. High levels of polybrominated diphenyl ethers in vacuum cleaner dust from California fire stations. Environ. Sci. Technol. 49 (8), 4988–4994.

Sjödin, A., Carlsson, H., Thuresson, K., Sjölin, S., Bergman, A., Ostman, C., 2001. Flame retardants in indoor air at an electronics recycling plant and at other work environments. Environ. Sci. Technol. 35 (3), 448–454.

Stapleton, H.M., Allen, J.G., Kelly, S.M., Konstantinov, A., Klosterhaus, S., Watkins, D., McClean, M.D., Webster, T.F., 2008. Alternate and new brominated flame retardants detected in U.S. house dust. Environ. Sci. Technol. 42 (18), 6910–6916.

Stapleton, H.M., Klosterhaus, S., Eagle, S., Fuh, J., Meeker, J.D., Blum, A., Webster, T.F., 2009. Detection of organophosphate flame retardants in furniture foam and U.S. house dust. Environ. Sci. Technol. 43 (19), 7490–7495.

Stapleton, H.M., Sharma, S., Getzinger, G., Ferguson, P.L., Gabriel, M., Webster, T.F., Blum, A., 2012. Novel and high volume use flame retardants in US couches reflective of the 2005 PentaBDE phase out. Environ. Sci. Technol. 46 (24), 13432–13439.

Suarez-Lopez, J.R., Jacobs Jr, D.R., Himes, J.H., Alexander, B.H., Lazovich, D., Gunnar, M., 2012. Lower acetylcholinesterase activity among children living with flower plantation workers. Environ. Res. 114, 53–59.

U. S. EPA, 2014. Technical Fact Sheet - Polybrominated Diphenyl Ethers (PBDEs) and Polybrominated Biphenyls (PBBs). U. S. Environmental Protection Agency, Washington, DC EPA 505-F-14-006.

Van den Eede, N., Dirtu, A.C., Neels, H., Covaci, A., 2011. Analytical developments and preliminary assessment of human exposure to organophosphate flame retardants from indoor dust. Environ. Int. 37 (2), 454–461.

Van den Eede, N., Dirtu, A.C., Ali, N., Neels, H., Covaci, A., 2012. Multi-residue method

for the determination of brominated and organophosphate flame retardants in indoor dust. Talanta 89, 292–300.
van der Veen, I., de Boer, J., 2012. Phosphorus flame retardants: properties, production, environmental occurrence, toxicity and analysis. Chemosphere 88 (10), 1119–1153.
Walton, S.M., Conrad, K.M., Furner, S.E., Samo, D.G., 2003. Cause, type, and workers' compensation costs of injury to fire fighters. Am. J. Ind. Med. 43 (4), 454–458.
Webber, M.P., Glaser, M.S., Weakley, J., Soo, J., Ye, F., Zeig-Owens, R., Weiden, M.D., Nolan, A., Aldrich, T.K., Kelly, K., Prezant, D., 2011. Physician-diagnosed respiratory conditions and mental health symptoms 7-9 years following the world trade center disaster. Am. J. Ind. Med. 54 (9), 661–671.
Whitehead, T., Metayer, C., Buffler, P., Rappaport, S.M., 2011. Estimating exposures to indoor contaminants using residential dust. J. Expo. Sci. Environ. Epidemiol. 21 (6), 549–564.
Whitehead, T.P., Brown, F.R., Metayer, C., Park, J.S., Does, M., Petreas, M.X., Buffler, P.A., Rappaport, S.M., 2013. Polybrominated diphenyl ethers in residential dust: sources of variability. Environ. Int. 57–58, 11–24.
Wobst, M., Wichmann, H., Bahadir, M., 1999. Surface contamination with PASH, PAH and PCDD/F after fire accidents in private residences. Chemosphere 38 (7), 1685–1691.
Zota, A.R., Rudel, R.A., Morello-Frosch, R.A., Brody, J.G., 2008. Elevated house dust and serum concentrations of PBDEs in California: unintended consequences of furniture flammability standards? Environ. Sci. Technol. 42 (21), 8158–8164.