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Flame retardants, dioxins, and furans in air and on firefighters' protective ensembles during controlled residential firefighting

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ABSTRACT

Introduction: Structure fires that involve modern furnishings may emit brominated flame retardants (BFRs) and organophosphate flame retardants (OPFRs), as well as brominated and chlorinated dioxins and furans, into the environment.

Objectives: The goal of this study was to quantify the airborne and personal protective equipment (PPE) contamination levels of these compounds during controlled residential fires in the U.S., and to evaluate gross-decontamination measures.

Methods: Bulk-sampling was done to confirm the presence of flame retardants (FRs) in the furnishings used in 12 controlled residential structure fires. Area air samples were collected during the fires and PPE wipe samples were collected from the firefighters' turnout jackets and gloves after firefighting. For each fire, half of the jackets were decontaminated and the other half were not.

Results: Of the BFRs and OPFRs measured in air during the fire period, decabromodiphenyl ether (BDE-209) and triphenyl phosphate (TPP) were the most abundant, with medians of 15.6 and 408 $\mu\text{g}/\text{m}^3$, respectively, and were also detected during overhaul. These and several other BFRs and OPFRs were measured on PPE. Some gloves had contaminant levels exceeding 100 ng/cm^2 and were generally more contaminated than jackets. Air and surface levels of the brominated furans appeared to be higher than the chlorinated dioxins and furans. Routine gross decontamination appeared to reduce many of the BFR contaminants, but results for the OPFRs were mixed.

Conclusions: Structure fires are likely to result in a variety of FRs, dioxins, and furans into the environment, leading to PPE contamination for those working on the fireground. Firefighters should wear self-contained breathing apparatus during all phases of the response and launder or decontaminate their PPE (including gloves) after fire events.

1. Introduction

Firefighters appear to have an increased risk of developing certain types of cancer (Daniels et al., 2014; Tsai et al., 2015). Chemical exposures encountered during or after firefighting may contribute to the increased cancer risk and could play a role in other chronic conditions among firefighters (Tsai et al., 2015).

While studies have found a variety of flame retardants (FRs) and other contaminants on turnout gear and in fire station dust (Alexander

and Baxter, 2016; Easter et al., 2016; Mayer et al., 2019; Shen et al., 2015), we are not aware of any studies that have measured the airborne levels of thermally released FRs and combustion byproducts (i.e. brominated and chlorinated dioxins and furans) during structural firefighting or investigated how this relates to personal protective equipment (PPE) contamination. Exposure to different types of FRs is a concern during structural firefighting because of their presence in upholstered furniture, carpet padding, electronics, and other consumer products that may contribute to the fuel load of the fire and because of

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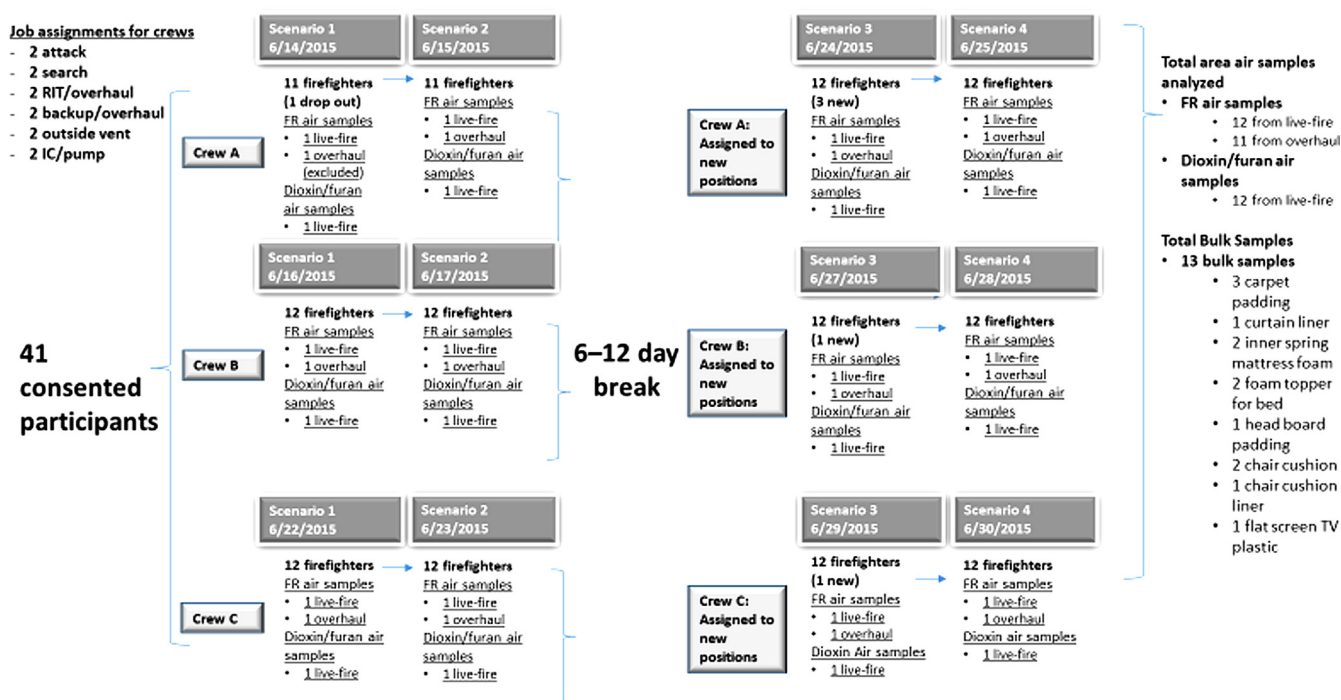


Fig 1. Study design and air and bulk sampling strategy.

their known detrimental health effects.

Polychlorinated diphenyl ethers (PBDEs) have been in use since the 1970s and were the primary class of commercial FRs prior to 2005 (Behl et al., 2016). PBDEs are environmentally persistent and can remain structurally unchanged on surfaces (including turnout gear) for long periods of time (e.g., years) (Alexander and Baxter, 2016; Easter et al., 2016). The Stockholm Convention added penta- and octa-formulations of PBDE mixtures to the Persistent Organic Pollutants (POPs) list in 2009, and then later added the deca-formulation in 2017 (United Nations Environment, 2017), but also provided exemptions for recycling and reusing products containing PBDEs until 2030 (DiGangi and Strakova, 2011). Additionally, firefighters may continue to be exposed to PBDEs for years to come due to their presence in products with relatively long lifespans (e.g., furniture).

The use of two classes of FRs has increased as a result of PBDE's addition to the POPs list: organophosphate flame retardants (OPFRs) and non-PBDE brominated flame retardants (NPBFRs), which have been used in a variety of household items, ranging from furniture to textiles (Dishaw et al., 2011; NIEHS, 2018). In addition to FRs, there are potentially hundreds of brominated and chlorinated, and mixed brominated and chlorinated dioxins and furans in any given combustion event (Birnbaum et al., 2003; Bjurlid et al., 2017; Zhang et al., 2016).

Exposure assessment studies have measured elevated metabolite levels of certain PBDEs (e.g., BDE-209 and BDE-47), OPFRs (e.g., tris (1,3-dichloropropyl) phosphate [TDCPP] and triphenyl phosphate [TPP or TPhP], a plasticizer with FR properties), and chlorinated and brominated dioxins and furans in biological specimens of firefighters (Dishaw et al., 2011; Jayatilaka et al., 2017; Shaw et al., 2013). Exposure to these compounds has been linked to a variety of adverse health effects, including neurotoxicity, cytotoxicity, immunotoxicity, and endocrine disruption (Behl et al., 2016; Birnbaum et al., 2003; Dishaw et al., 2011; Linares et al., 2015; Park et al., 2015; Saunders et al., 2013). The carcinogenicity of FRs is largely unknown. However, one study found an association between BDE-209 (as well as tris (2-chloroethyl) phosphate [TCEP]) and papillary thyroid cancer (Hoffman et al., 2017). As for dioxins and furans, the International Agency for Research on Cancer (IARC) has designated 2,3,7,8-tetrachlorodibenzo-para-dioxin and 2,3,4,7,8-pentachlorodibenzofuran as carcinogenic to humans (Group

1) (IARC, 2012).

The purpose of this study was to characterize the airborne and PPE surface contamination levels of FRs, dioxins, and furans during controlled realistic residential fire responses. We also designed the study to explore the effectiveness of gross on-scene decontamination, also known as preliminary exposure reduction, at removing different types of FRs from turnout gear. Our goal was to provide decision makers in the fire service with practical information to better understand and reduce firefighters' exposures to these compounds, which in turn, should also reduce the potential for adverse health effects.

2. Methods

2.1. Experimental procedure and study design

The experimental procedure and study design are described in detail elsewhere (Fent et al., 2017; Fent et al., 2018; Horn et al., 2018). The fires took place inside a 111 m² wood-frame residential structure (Supplemental Fig. S1) with gypsum board wall/ceiling linings and typical residential furnishings acquired from a hotel surplus store – making sure to select identical (or nearly identical) used furnishings for all 12 fires. The two bedrooms where the fires were ignited were furnished with a double bed (covered with a new foam mattress topper, comforter, and pillow), stuffed chair, side table, lamp, dresser, and flat screen television. The floors were covered with rebonded polyurethane foam padding and new polyester carpet. Ignition was accomplished by electronically igniting a book of matches on top of a chair adjacent to the bed in each bedroom. After ignition, the fires were allowed to grow until the rooms approached flash-over conditions and became ventilation limited (typically 4–5 min) and then the firefighters were dispatched. Peak air temperatures in both bedrooms reached in excess of 600 °C from floor to the ceiling with temperatures exceeding 1000 °C in some scenarios (Horn et al., 2018).

A crew of twelve firefighters, wearing brand-new turnout jackets, pants, and gloves, were paired up by job assignment to carry out a coordinated attack of a controlled residential fire, which was repeated the next day using a different attack tactic (while wearing the same gear). Approximately one week later, the returning firefighters were

Table 1
PPE (jacket and glove) wipe samples collected after the last of 4 fire scenarios.

	Decon	No Decon	Decon	No Decon
Job assignments across 4 fire scenarios	Attack, Search, Outside Vent, and Overhaul	Attack, Search, Outside Vent, and Overhaul	Overhaul/IC/Engineer	IC/Engineer
# of FR samples from jackets ^a	5	5	1	1
# of FR samples from right-handed gloves ^b	N/A	7	N/A	N/A
# of Dioxin and Furan samples from left-handed gloves ^b	N/A	7	N/A	N/A

^a Wipe samples of jackets were taken from 12 participants from one of the three crews (Crew C).

^b Wipe samples of gloves were taken from 3 participants from each of the three crews (Crews A, B, and C). Nine total samples were collected, but two were lost during transport and were excluded from the analysis.

reassigned to new positions and repeated this experiment (while wearing the same gear) (Fig. 1). This was done on total of three crews (12 firefighters per crew, 4 burns per crew). The five firefighters unable to return a week later were replaced with new participants (resulting in a total of 41 participants). These new participants were given new or previously worn gear depending on availability and size.

Firefighters assigned to 'Attack' pulled a primary hoseline and suppressed all active fire. 'Search' firefighters performed forcible entry into the structure and searched for and rescued two simulated victims (75 kg mannequins). 'Outside Vent' firefighters created openings in the windows and roof to ventilate the structure. The incident commander ('IC') and pump operator ('Engineer') completed typical exterior operations on the fireground, but never worked inside or on the fire building. Firefighters assigned to 'Overhaul' were stationed outside the structure during active fire either holding a secondary line (backup) or as a rapid intervention team (RIT). The attack team and IC determined when the fire had been suppressed, at which time, attack and search firefighters exited the structure and overhaul firefighters entered the structure to search for and suppress any smoldering items in the fire rooms, walls, and ceilings.

Immediately after completion of the assigned task, the firefighter walked to an open bay where PPE was removed, turnout jackets hung in individual lockers and firefighting gloves placed on a shelf. Of the 12 jackets, six were designated for gross on-scene wet-soap decontamination after each scenario (Fent et al., 2017). Briefly, the investigator prepared a 7.6 L pump sprayer filled with a mixture of ~6L of water and ~10 mL of Dawn® dish soap (Procter and Gamble). The investigator pre-rinsed the gear with water, sprayed the gear with the soap mixture, scrubbed the gear with soap mixture using an industrial scrub brush, rinsed the gear with water until no more suds remained, and then hung the gear to dry overnight (Fent et al., 2017). Gloves were not decontaminated between scenarios. Turnout jackets that were not designated for decontamination were hung up and allowed to air out. Gear remained in the bay until it was donned for the next scenario. Approximately 24 hr transpired between the first two and last two scenarios, and ~1 week transpired between the 2nd and 3rd scenario, where firefighters (and their gear) received new assignments. Hence, each set of gear was typically worn in four different scenarios, and either decontaminated four times or never decontaminated. This provided a means for comparing contamination levels between routinely decontaminated turnout gear and turnout gear without any decontamination. These exposures were considered representative of an active fire department engaged in structural fire suppression activities.

2.2. Bulk sampling of fuel package

A total of 13 bulk samples of the furnishings were collected (Fig. 1) before combustion over two separate periods (at the beginning and end of the study). Samples were collected by cutting out at least 25 cm² pieces from the items by using pre-cleaned scissors or a utility knife while wearing nitrile gloves.

2.3. Area air sampling

Fig. 1 outlines the area air sampling design. The air sampling procedure is described in detail in Fent et al. 2018. Briefly, the sampling trains were located on the outside of the structure and protected by an insulated cooler during the fires. Tygon tubing (~1.3 m in length, 0.64 cm internal diameter) connected to the inlet of the sampling media (located in the cooler) were used to draw air from the fire structure through a hole ~0.9 m above the living room floor, approximating firefighters' crawling/crouching height. The tubing was wrapped in fiberglass insulation to minimize condensation losses. This method was developed to protect the sampling media from hot gases and water.

After fire suppression was complete, overhaul firefighters began entering the structure and another set of sampling trains were attached to the exterior wall of the structure. Sampling media was inserted through the pre-drilled hole in the wall of the bedroom where the fire was ignited. This hole was 1.8 m above the floor to approximate standing height. The pumps were promptly started and ran until a few minutes after the overhaul firefighters exited the structure.

For the FRs, SKC Inc. OVS XAD-2 tubes (1 µm glass fiber filter and XAD-2 sorbent with glass wool separators) were used to sample the air at a flow rate of 1 L/min. The same sample media was used to sample the air for dioxins and furans but at a flow rate of 2.5 L/min. The filter and XAD sorbent were analyzed together for all samples, except for three FR air samples collected during the last three scenarios. Additional analysis was done on those three air samples to investigate the solid/vapor phase partitioning of the FRs.

2.4. Surface wipe sampling

Table 1 provides the study design for wipe samples taken from PPE. Briefly, the outside of the firefighting gloves and turnout jackets were sampled for FRs. Cotton twill wipes soaked in 99% isopropanol were used to wipe the front of the turnout jackets using a 10 cm × 10 cm template as a guide. A similar surface area was approximated by wiping the entire palm side of the right-handed gloves. Collections were performed on nine gloves and 12 jackets after the last of the four live-fire scenarios. Investigators wore nitrile gloves during the collections.

Left-handed gloves were also sampled for dioxins and furans using 100 cm² cotton gauze pads, which were previously cleaned with dichloromethane, air dried, and pre-wetted with hexane using the same collection method as previously described. Samples were collected from nine gloves after the last of the four fire scenarios. Gloves were not decontaminated during the course of the study.

2.5. Chemical analyses

Air, wipe, and bulk samples were analyzed for BFRs and chlorinated and non-chlorinated OPFRs using ultra-performance liquid chromatography (UPLC)-atmospheric pressure photoionization (APPI) tandem mass spectrometry as previously described (La Guardia and Hale, 2015). Air samples were also analyzed for chlorinated dioxins and

Table 2Air concentrations of flame retardants ($\mu\text{g}/\text{m}^3$) during active fire and overhaul periods. ND values were replaced by LOD/2 (divided by air volume).

Analyte	Fire Period (N = 12) ^d				Overhaul Period (N = 11)			
	Median ^c	Range	N of samples detected	LOD/2 Range	Median ^c	Range	N of samples detected	LOD/2 Range
PBDEs^a								
BDE-47	3.47	0.07–13.9	8	0.07–0.15	0.02	0.02–0.39	1	0.02–0.03
BDE-99	4.94	0.03–13.8	10	0.03–0.08	0.02	0.02–0.12	1	0.02–0.03
BDE-153	–	–	–	–	0.02	0.02–0.40	1	0.02–0.03
BDE-154	0.09	0.03–12.7	1	0.03–0.24	–	–	–	–
BDE-206	0.08	0.03–4.50	1	0.03–0.24	–	–	–	–
BDE-209	15.6	0.03–67.7	9	0.03–0.13	1.08	0.02–29.4	9	0.02
NPBFRs								
TBBPA	0.24	0.03–18.5	5	0.03–0.24	–	–	–	–
TBB	7.71	0.08–25.2	11	0.08	0.03	0.02–26.5	4	0.02–0.03
TBPH	0.86	0.03–3.65	9	0.03–0.24	0.02	0.02–7.01	2	0.02–0.03
DBDPE	0.08	0.03–2.18	2	0.03–0.24	0.02	0.02–1.41	2	0.02–0.03
OPFRs^b								
TDCPP	0.12	0.05–4.04	1	0.05–0.36	–	–	–	–
TDCPP	0.13	0.05–113	2	0.05–0.36	–	–	–	–
TPP	408	0.02–2110	11	0.02	2.81	1.07–45.8	11	–
TCP	0.04	0.01–897	4	0.01–0.05	0.01	0.004–13.9	4	0.004–0.006

^a BDE-85, BDE-100, and BDE-183 were not detected for fire period and overhaul period.^b TCEP was not detected for fire period and overhaul period.^c Reported medians for analytes with less than 50% detection rate are heavily influenced by the imputed levels. Caution should be exercised in interpreting these results.^d Due to extreme conditions, air samples ran for 4–14 min of the fire period (which lasted 15–18 min).

furans using EPA Method 23A (EPA, 1997), modified by using OVS-XAD-2 tubes for sampling media. Wipe samples were analyzed for chlorinated dioxins and furans using EPA Method 8290A (EPA, 2007), modified by using cotton gauze wipes soaked in hexane for sampling media. Both of the EPA methods use high resolution GC/high resolution MS. Extracts of these wipe and air samples were stored at $-20\text{ }^\circ\text{C}$ and were analyzed approximately 1-year later for brominated dioxins and furans using a gas chromatograph coupled with a single quadrupole low resolution mass spectrometer operated in electron ionization mode. Additional details on this analytical method are provided in the Supplemental Materials.

2.6. Data analysis

Summary statistics were presented as median and range for the variables of interest. In calculating the descriptive statistics, non-detectable air concentrations and PPE contamination levels of FRs, and brominated and chlorinated dioxins and furans were assigned values using the limits of detection (LOD) divided by 2 because the data were highly skewed (Hornung and Reed, 1990). For highly censored data (more than 50% non-detected), only the detectable air concentrations and PPE contamination levels were reported and shown on graphs with dots. Box and whisker plots with minimum, 25th percentile, median, 75th percentile, and maximum were performed for the concentrations detected greater than and equal to 50%.

A Wilcoxon rank-sum test was utilized to determine air concentration differences of FRs between fire and overhaul periods and PPE contamination levels of FRs detected in the wipe samples between turnout jackets and gloves post-firefighting. To quantify the effectiveness of routine gross on-scene decontamination, a Wilcoxon signed-rank test was utilized to examine whether the change in FR contamination on the routinely decontaminated vs. non-decontaminated jackets by last job assignment was significantly different from zero, excluding when the comparison decontaminated and non-decontaminated jackets had zero contamination. All tests were two-sided at the 0.05 significance level. Statistical analyses were conducted in SAS version 9.4 (SAS Institute, Cary, NC).

3. Results

Supplemental Tables S1-S3 provide the abbreviations used for the FR analytes and brominated and chlorinated dioxins and furans, many of which are better known by their abbreviations.

Lab blanks and field blanks were analyzed for all samples, except for the bulk samples, and resulted in non-detectable concentrations for the analytes of interest with only a few exceptions for the chlorinated dioxins and furans as noted in the ensuing tables. Quality control analyses were performed for all analytes. The FR results were corrected by the surrogate standard recoveries. The vast majority of chlorinated dioxin and furan recoveries were within 80–120% of the spiked amounts and were not corrected. Surrogate standards for the brominated dioxins and furans were below the detection limits, so these results should be considered qualitative.

3.1. Concentrations of FRs in furnishings

Supplemental Table S4 summarizes the FR concentrations in the fuel packages used for the fires. All FRs of interest in this study, except TCP and TBBPA, were detected in at least one furnishing item that was sampled, indicating that a source existed for nearly all FRs being evaluated. Although an effort was made to have identical furnishings for all scenarios, the FR composition in the furnishings likely varied across the 12 fires. Because bulk sampling of the furnishings was only conducted at the beginning and end of the study, these results may not represent the FR composition across all 12 fires.

3.2. Air concentrations of FRs, and brominated and chlorinated dioxins and furans

Table 2 summarizes the air concentrations of FRs measured during the fire and overhaul periods. As expected, the compounds of interest were detected more frequently and their concentrations were generally much higher during the fire period than during overhaul. For example, the median fire-period concentrations of BDE-209 ($15.6\text{ }\mu\text{g}/\text{m}^3$) and TPP ($408\text{ }\mu\text{g}/\text{m}^3$) were more than an order of magnitude higher than their air concentrations during overhaul (1.08 and $2.81\text{ }\mu\text{g}/\text{m}^3$, respectively); corresponding Wilcoxon rank-sum p-values were 0.053 and

0.001). We performed Pearson correlation analysis for the two most-detected compounds by phase of the response and found that the BDE-209 concentrations were highly correlated between the fire and overhaul periods ($r = 0.78$), while the TPP concentrations were moderately correlated between the fire and overhaul periods ($r = 0.48$). This suggests that higher emissions of these compounds during the fires led to higher air concentrations during the overhaul periods.

To explore the gas/solid phase partitioning of the FRs in air, the filter and sorbent were analyzed separately for three of the fire-period air samples (Supplemental Table S5). Several compounds were only detected in one or two of the samples, making interpretation of the data difficult. For chemicals that were detected in 100% of the samples, BDE-99 and TBB existed predominately as particulate (> 85% solid phase), TPP was mostly particulate (64% solid phase), and BDE-209 was mostly in gas phase (25% solid phase). While the latter finding is somewhat surprising because BDE-209 has a lower vapor pressure than other PBDEs (i.e., BDE-99), there are several factors that could impact partitioning into vapor, including how the different FRs were incorporated into the furnishing materials (e.g., added during polymerization or as a surface treatment).

Supplemental Fig. S2 summarizes the qualitative air concentrations of the brominated dioxins and furans measured during the fire period. Only two brominated furans (an unknown tetrabromodibenzofuran homologue, first to elute in chromatography, and an unknown pentabromodibenzofuran homologue, first to elute in chromatography) were detected in more than 50% of the samples, with respective median values of 8.17 and 2.30 $\mu\text{g}/\text{m}^3$. In addition, Supplemental Fig. S3 summarizes the air concentrations of the chlorinated dioxins and furans measured during the fire period. While the detection rate of the chlorinated dioxins and furans was higher than the brominated dioxins and furans, median values were much lower, ranging from 0.00018 to 0.0011 $\mu\text{g}/\text{m}^3$.

3.3. PPE contamination levels of FRs, and brominated and chlorinated dioxins and furans

The levels of FRs measured on turnout jackets post-firefighting are summarized in Table 3. For gear that was not decontaminated, BDE-209 was the most abundant BFR found on the jackets and was measured at concentration levels ranging from 19.7 ng/cm^2 to 47.4 ng/cm^2 . TDCPP and TPP were the most abundant OPFRs found on the jackets. Concentration levels of TDCPP ranged from 0.8 ng/cm^2 to 38.8 ng/cm^2 , while TPP ranged from 4.8 ng/cm^2 to 93.5 ng/cm^2 (for jackets that were not decontaminated). Interestingly, detectable levels of six different FRs (including BDE-209 and TPP) were found on the IC/engineer's turnout gear that was not decontaminated, even though this jacket never passed the threshold of the fire building. Each of the detected FR concentrations on this jacket are well below the median contamination on gear from the other fireground tasks (e.g. BDE-209 was 78% lower, TPP was 83% lower).

The levels of FRs measured on right-handed gloves post-firefighting are summarized in Table 4. Firefighters appeared to have higher BDE-209, TBB, and DBDPE contaminations on their gloves than jackets (Wilcoxon $P = 0.054$, 0.027, and 0.003, respectively). However, a direct comparison cannot be made because the jackets and gloves in this comparison were not worn by exactly the same people.

The left-handed gloves were tested for brominated and chlorinated dioxins and furans (Tables S6 and S7). Compared to the air samples, the detection frequency of brominated furans was higher for the gloves. Conversely, chlorinated dioxins and furans were detected less frequently on gloves than in air. Several brominated furans were detected in > 85% of the collected wipe samples. Like the air samples, an unknown tetrabromodibenzofuran homologue, first to elute in chromatography, was the most abundant contaminant found (median 8.0 ng/cm^2 and range from 0.2 to 23.7 ng/cm^2).

3.4. Effectiveness of routine gross on-scene decontamination

The difference in FR contamination between routinely decontaminated and not-decontaminated jackets suggests the wet soap decontamination approach has mixed effectiveness (Table 3). Several of the FRs were not detected in either of the jacket conditions, and so, we could not estimate the effectiveness of decontamination for those particular compounds (e.g., BDE-183, TCEP). For those FRs that were detected, we had low power to detect statistical differences at a 0.05 level. In addition, a major assumption of this study is that two sets of gear (subjected or not subjected to routine gross on-scene decontamination) would have had similar levels of FR contaminants had the gear been worn for the same job assignments. This assumption is not without potential bias, particularly with respect to between-worker variability that is known to occur in industry. In addition, we did not test the gear before being used in fires to determine if any FRs were present—perhaps as part of the manufacturing process. Nevertheless, many of the PBDEs were consistently lower in the routinely decontaminated jackets. For example, BDE-209, which was among the most abundant contaminants, was a median of 15 ng/cm^2 or 49% lower in the routinely decontaminated jackets, with a range of differences (decontaminated minus not decontaminated) that were all negative. However, TDCPP, which was also among the most abundant contaminants, appeared to be higher on several of the routinely decontaminated jackets.

Firefighters assigned to IC and engineer were *a priori* considered unlikely to have substantial contamination on their turnout gear from firefighting. Therefore, we considered their wipe-sampling results separately from the other groups. Interestingly, all but one of the compounds (detected in at least one of the two samples) were higher in the samples collected from the IC/Engineer's routinely decontaminated jackets than the non-decontaminated jackets. However, this could have been due to the IC/engineer's disparate previous job assignments. In particular, the IC/engineer whose gear was decontaminated was previously assigned to RIT/overhaul; while the IC/engineer whose gear was not decontaminated was previously also assigned to IC/engineer for the first two scenarios. It is likely that accumulated contamination from prior mixed exposures contributed to difficulties in making distinctions between fireground assignments and the use of gross decontamination.

4. Discussion

While every residential fire will vary, this study was designed to replicate conditions commonly encountered by structural firefighters, where foams, plastics, and textiles of different types, quantities, and ages are involved in the fire. This study is the first to show that FRs in residential furnishings can be released into the fire environment and deposited onto firefighters' PPE during combustion events, including PBDEs that have been phased out of production but are still present in many buildings throughout the United States. We measured detectable levels of a variety of BFRs and OPFRs in the air inside the structure during the fires, with some compounds persisting at detectable levels in air during overhaul (e.g., TPP and BDE-209). Most of these compounds existed as particulate (or absorbed onto particulate) and were further quantified on firefighters' PPE. In addition, we detected several brominated and chlorinated dioxins and furans in the fire environment air and on PPE.

During the fire period, median air concentrations of BDE-209 (15.6 $\mu\text{g}/\text{m}^3$) were 3-fold higher than any other PBDE, and TPP (408 $\mu\text{g}/\text{m}^3$) was 3000-fold higher than any other OPFR. A recent study reported FR air concentrations from multiple industries and found substantially lower BDE-209 concentrations in personal air samples taken from electronic waste facility workers (median = 0.060 $\mu\text{g}/\text{m}^3$) (Estill et al., 2020). Estill et al. (2020) also reported TPP air concentrations for workers at a chemical manufacturing facility that were orders of magnitude lower than the current study. In fact, median BDE-

Table 3

FR concentrations measured (ng/cm²) from jackets with and without any decontamination after completion of 4 scenarios involving a combination of the following fireground tasks: fire attack, search, outside vent, and overhaul. For comparison, we also provide FR concentrations measured from jackets with decontamination after completion of overhaul and IC/engineer tasks and without decontamination after IC/engineer tasks only across the 4 fire scenarios. ND values were replaced by LOD/2.

Analyte	Attack, Search, Outside Vent, and Overhaul						P-value ^d	IC/Engineer, No Decon (N = 1)	Overhaul, IC/Engineer Routine Decon (N = 1)	LOD/2
	No Decon (N = 5)			Routine Decon (N = 5)						
	Median ^c	Range	N of samples detected	Median ^c	Range	N of samples detected				
PBDEs^a										
BDE-47	1.70	0.86–3.04	5	0.05	0.05–0.45	2	0.063	–	1.59	0.05
BDE-99	2.19	0.56–3.97	5	0.05	0.05–0.50	1	0.063	0.34	1.27	0.05
BDE-100	0.29	0.05–0.65	4	0.05	–	0	–	–	0.39	0.05
BDE-153	0.05	0.05–0.39	2	0.05	–	0	–	–	0.27	0.05
BDE-154	0.05	0.05–0.63	1	0.05	–	0	–	–	0.53	0.05
BDE-206	0.05	0.05–2.61	1	0.05	0.05–0.63	1	–	–	–	0.05
BDE-209	30.7	19.7–47.4	5	15.7	5.23–29.0	5	0.063	6.83	6.50	0.05
NPBFRs										
TBBPA	0.05	0.05–7.60	2	0.05	0.05–0.75	1	0.500	–	–	0.05
TBB	0.58	0.20–3.11	5	0.47	0.29–0.86	5	0.625	–	0.26	0.05
TBPH	0.50	0.31–1.28	5	0.37	0.05–0.78	4	0.813	0.24	0.25	0.05
DBDPE	0.18	0.05–1.45	3	0.05	–	0	–	–	–	0.05
OPFRs^b										
TCPP	0.78	0.78–13.6	1	0.78	–	0	–	–	–	0.78
TDCPP	7.54	0.78–38.8	4	39.3	0.78–79.7	4	0.188	0.99	5.56	0.78
TPP	20.0	4.79–93.5	5	5.55	2.47–12.3	5	0.313	3.42	4.50	0.05
TCP	0.88	0.55–1.28	5	0.05	0.05–1.25	2	0.625	0.52	0.96	0.05

^a BDE-85 and BDE-183 were not detected in any samples.

^b TCEP was not detected in any samples.

^c Reported medians for analytes with less than 50% detection rate are heavily influenced by the imputed levels. Caution should be exercised in interpreting these results.

^d A Wilcoxon signed-rank test was utilized to examine whether the change in FR levels after decontamination procedures was significantly different from zero. Note that small sample size might result in insufficient statistical power to detect differences at the 0.05 significance level.

Table 4

FR concentrations measured (ng/cm²) from right-handed gloves without any decontamination after completion of 4 scenarios involving a combination of the following fireground tasks: fire attack, search, outside vent, overhaul. ND values were replaced by LOD/2.

Analyte	Attack, Search, Outside Vent, and Overhaul (N = 7)			
	Median ^b	Range	N of samples detected	LOD/2
PBDEs^a				
BDE-47	2.36	0.27–5.06	7	–
BDE-99	3.34	0.32–7.59	7	–
BDE-100	0.05	0.05–1.70	3	0.05
BDE-153	2.68	0.05–4.02	6	0.05
BDE-154	0.05	0.05–3.42	1	0.05
BDE-183	0.05	0.05–8.09	3	0.05
BDE-206	8.58	0.05–19.1	6	0.05
BDE-209	74.8	9.06–148	7	–
NPBFRs				
TBBPA	0.05	0.05–0.53	2	0.05
TBB	10.2	0.24–296	7	–
TBPH	4.94	0.11–116	7	–
DBDPE	12.5	2.29–30.5	7	–
OPFRs				
TCEP	0.78	0.78–40.1	1	0.78
TCPP	1.45	0.78–602	4	0.78
TDCPP	3.40	0.78–31.2	4	0.78
TPP	20.6	0.05–157	5	0.05
TCP	0.05	0.05–4.31	2	0.05

^a BDE-85 was not detected in any samples.

^b Reported medians for analytes with less than 50% detection rate are heavily influenced by the imputed levels. Caution should be exercised in interpreting these results.

209 concentrations during overhaul from the current study were still orders of magnitude higher than concentrations reported in [Estill et al. \(2020\)](#). To our knowledge, TPP and BDE-209 air concentrations in this study are the highest reported in the literature to date.

BDE-209, TDCPP, and TPP were the most abundant compounds measured on jackets, with levels ranging up to 47.4, 38.8, and 93.5 ng/cm², respectively. These compounds were also abundant on gloves, with BDE-209 and TPP being measured at levels ranging up to 148 and 157 ng/cm², respectively. In addition, TCPP and TBB were measured on gloves at maximum levels of 602 and 296 ng/cm², respectively; although, their medians were much less than BDE-209 and TPP. We previously measured FR contamination in used firefighting hoods (from the same study) and found that BDE-209 and TPP were the most abundant PBDE and OPFR contaminants ([Mayer et al., 2019](#)). [Alexander and Baxter \(2016\)](#) found that BDE-209 and BDE-47 were the most abundant PBDE contaminants in used gloves and hoods. [Easter et al. \(2016\)](#) found that BDE-99 was the most abundant PBDE measured in the outer shell of used turnout jackets; however, this study did not analyze for BDE-209. These previous studies employed destructive bulk sampling and cannot be compared directly to our measurements. However, Easter et al. interpolated the 95th percentile surface loading for BDE-99 of 100 ng/cm², which is within the range of levels found in this study for the most abundant contaminants (i.e., BDE-209 and TPP).

Interestingly, many of these same compounds (BDE-209, TDCPP, and TPP) have been measured in the dust of U.S. fire stations at levels well above those measured in homes or other occupational settings ([Shen et al., 2018](#); [Shen et al., 2015](#)). Likewise, previous biomonitoring studies have found elevated metabolite levels of these compounds in firefighters. For example, by comparing to general population levels, researchers have found 2 to 3-fold higher levels of PBDE metabolites in firefighters' serum, with BDE-209 being the most dominant species (constituting > 30% of the total serum concentrations) ([Shaw et al.,](#)

2013), and 3 to 10-fold higher urinary metabolites of TCEP, TCPP, TDCPP, and TPP among recently exposed firefighters (Jayatilaka et al., 2017).

Dioxins and furans are combustion byproducts (not thermally liberated parent compounds like FRs) and as such, would be heavily influenced by environmental conditions (temperature, ventilation, humidity, etc.) as well as the fuel package (Zhang et al., 2016). The brominated dioxin and furan data collected for this project should be considered qualitative and exploratory due to the use of low-resolution GC/MS for analysis. Nevertheless, our findings suggest that brominated furans may be of greater concern for firefighters than chlorinated dioxins and furans due to their relatively higher contamination levels in air and on PPE surfaces. These findings likely depend on the bromine and chlorine content of the fuel package, and additional research is certainly warranted.

Firefighters could inhale these compounds emitted into the air if they were not wearing SCBA while downwind of the structure fire or if they were to remove their SCBA while inside the structure during overhaul. However, air concentrations at these locations and time periods would likely be much lower than what we reported inside the structure during active fire. In addition, more progressive departments have policies requiring the use of SCBA during activities where exposures are likely, such as during overhaul. However, even if SCBA is worn, the results in this study suggest another potential exposure route. Many of the FRs, dioxins, and furans are persistent and could transfer to the skin upon subsequent use of PPE or penetrate the PPE through interface elements during firefighting and directly contact the skin.

Limited data exists on the permeability of these compounds through skin. However, an in-vitro study found faster permeation for lower brominated PBDEs (typically with lower octanol/water coefficients [$\log K_{ow}$]) and greater accumulation in the epidermis for higher brominated PBDEs (e.g., BDE-209) (Abdallah et al., 2015). Likewise, two ex-vivo skin penetration studies indicated generally decreasing permeability with increasing $\log K_{ow}$ and higher skin absorption of OPFRs (e.g., TCEP and TDCPP) compared to the NPBFRs (e.g., TBB and DBDPE) (Frederiksen et al., 2018). Chlorinated and brominated dioxins and furans similarly show an inverse correlation ($R^2 = 0.98$) between dermal penetration and $\log K_{ow}$ (Jackson et al., 1993). It should be noted that slower penetration through the skin could indicate a much slower release into the circulation rather than no potential for absorption (Frederiksen et al., 2018). Furthermore, contaminants that accumulate in the stratum corneum of the hands could be ingested, depending on the frequency and efficiency of hygiene practices.

Given the potential for dermal absorption or inadvertent ingestion, it is prudent that turnout gear be laundered after each exposure event. Gross on-scene decontamination using soap, water, and a scrub brush may be conducted before advanced cleaning (laundering). However, some departments only do gross on-scene decontamination and others do no on-scene decontamination after an exposure event.

We have previously shown that gross decontamination with soap and water is able to remove a median of 85% of PAH contamination from the surface of turnout gear (Fent et al., 2017). Here, we show that the effectiveness of this decontamination method may vary by type of FR. Many of the BFRs appear to be efficiently removed ($> 50\%$ less contamination on average), including BDE-209 which was the most abundant FR measured on turnout jackets. However, some of the OPFRs were not efficiently removed. For example, TDCPP was actually higher on average in the routinely decontaminated turnout jackets. The reason for this finding is unknown, but it is possible that the items used for decontamination (scrub brush, bucket) had become contaminated with TDCPP after continued use. If the decontamination tools had become contaminated, it makes sense that the hydrophilic OPFRs would be present in higher quantities on the wet tools than the hydrophobic BFRs. However, we did not see evidence of cross contamination for the other OPFRs.

In another study, we found that laundering was able to remove

much of the OPFR contamination (up to 98%) and NPBFR contamination (up to 44%) on previously used Nomex hoods, but these findings were not consistent across all compounds (Mayer et al., 2019). In particular, PBDE contamination levels were found to actually increase on hoods after laundering most likely due to cross contamination from other hoods during the laundry cycle (Mayer et al., 2019). These previous findings appear to contradict our results here. However, laundering is a different process than gross-decontamination and chemicals will have varying affinities for different types of textiles (Nomex vs. outer shell of turnout gear).

The fact that firefighters in this study performed two scenarios and then were reassigned to new positions for the last two scenarios is an important consideration in interpreting the findings. For example, the apparent increasing turnout-gear contamination after gross decontamination for the IC/engineer was most likely due to the fact that the IC/engineer whose gear was decontaminated had previously performed RIT/overhaul activities (during the first two scenarios), while the IC/engineer whose gear was not decontaminated was previously utilized in another IC/engineer role (Table 3), and hence, never worn inside the fire structure. This suggests three things: (1) PPE may be contaminated even if all firefighting activities are on the exterior of the structure, (2) exposures from the first two scenarios are an important factor in the contamination levels measured at the end of the study (more than a week later), and (3) gross decontamination was not able to return contamination levels to original background levels.

We previously reported higher PAH contamination on turnout jackets worn by firefighters performing fire attack and search operations after two consecutive scenarios than other job assignments (Fent et al., 2017). We might expect a similar finding with respect to FR contamination in this study, but due to the study design, we could not differentiate between specific job assignments. However, even though we lacked power to draw statistical conclusions, our results indicate that firefighters who performed a combination of attack, search, overhaul and outside vent activities (across 4 fire events) accumulated more toxicants on their gear than those assigned to IC or engineering tasks (Table 3).

Some of the highest contamination levels were measured on gloves, suggesting that in addition to the deposition of airborne particulate, the gloves can pick up contamination when firefighters crawl on the floor or handle partially burned or soot-covered items. While turnout jackets, trousers, and hoods are likely to be laundered more frequently today than in years past (depending on department policy and resources), gloves may not be laundered as frequently because the laundering process can change the fit, form, and dexterity of the gloves. Moreover, gloves are often the first items removed after firefighting without any gross decontamination, which may permit the transfer of contaminants to the hand skin.

5. Limitations

This study is not without limitations. The sampling method used for brominated dioxins and furans was qualitative and so the results should be considered exploratory. Our study design also did not allow us to fully evaluate exposure differences by job assignment—mainly because firefighters had more than one job assignment across the 4 fire scenarios and area air sampling was performed. Area air samples may not reflect the conditions surrounding the firefighters, which would have been better captured using personal air sampling. Due to the extreme environmental conditions, many of the sample pumps stopped 4–11 min before the culmination of the fire period. Hence, the fire period air concentrations may not accurately reflect the true time-weighted average air concentrations. Also, the use of tubing to draw air from the structure could have resulted in vapor condensation losses (as suggested in our previous study for PAHs) (Fent et al., 2018). However, the tubing was wrapped in insulation to minimize this effect. Another limitation of this study is that the wipe sampling methods utilized

common solvents (isopropanol and hexane) as wetting agents based on the advice of the analytical laboratories; however, to our knowledge, the collection efficiency of these wipes is unknown and could vary among the different compounds. Further research is needed to determine the collection efficiency of these wipes from turnout gear materials. We did not expect FRs to be present on the new turnout gear materials, but this cannot be completely ruled out and could explain why some FRs were detected even on the jacket worn only by IC/engineer (Table 3). Unfortunately, wipe samples were not collected before the fires to explore this possibility. Lastly, this was a relatively small study and we had insufficient power to explore all potential determinants of exposure or differences between job assignments.

6. Conclusions

Overall, this study demonstrates that firefighters can be exposed to BFRs, OPFRs, and brominated and chlorinated dioxins during structural firefighting. TPP and BDE-209 air concentrations reported in this study are the highest in the literature, although the magnitude of the airborne and PPE contamination levels will depend heavily on the types and quantities of items burning. Job assignment and environmental conditions may also play an important role, but these could not be fully evaluated in this study. That some FRs were detected during overhaul (e.g., BDE-209 and TPP) provides additional support for department policies requiring the use of SCBA during overhaul. Gross on-scene decontamination with soap and water appears to effectively remove some of the FR contaminants. However, a few of the OPFRs (e.g., TDCPP) appeared to be higher on the routinely decontaminated jackets, suggesting a potential for cross contamination. Hence, it may be worth considering the use of different brushes and buckets for firefighters whose gear is expected to have less contamination (e.g., IC/engineer). Gloves were contaminated with a variety of FRs, dioxins, and furans, often at a higher concentration than measured on jackets. This critical component of firefighting PPE should be removed in such a way as to minimize transfer of contaminants to skin. Gloves, like other turnout gear components, should be laundered following a live-fire event; however, more work is needed to determine the effectiveness of laundering for these compounds. Future work should investigate the biological absorption of these compounds after structural firefighting.

CRedit authorship contribution statement

Kenneth W. Fent: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing - original draft. **Mark LaGuardia:** Formal analysis. **Drew Luellen:** Formal analysis. **Seth McCormick:** Data curation, Writing - original draft. **Alexander Mayer:** Data curation. **I-Chen Chen:** Formal analysis. **Steve Kerber:** Methodology, Project administration, Supervision. **Denise Smith:** Conceptualization, Methodology, Funding acquisition, Investigation. **Gavin P. Horn:** Conceptualization, Methodology, Funding acquisition, Investigation, Project administration.

Declarations of Competing Interest

The authors declare that they have no competing financial interest in relation to the work described.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envint.2020.105756>.

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