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Characterizing exposures to flame retardants, dioxins, and furans among firefighters responding to controlled residential fires

Alexander C. Mayer [a,*], Kenneth W. Fent [a], I-Chen Chen [a], Deborah Sammons [b], Christine Toennis [b], Shirley Robertson [b], Steve Kerber [c], Gavin P. Horn [c,e], Denise L. Smith [d,e], Antonia M. Calafat [f], Maria Ospina [f], Andreas Sjodin [f]

[a] Division of Field Studies and Engineering, National Institute for Occupational Safety and Health (NIOSH), Centers for Disease Control and Prevention (CDC), Cincinnati, OH, USA
[b] Health Effects Laboratory Division, NIOSH, CDC, Cincinnati, OH, USA
[c] Firefighter Safety Research Institute, Underwriters Laboratories, Columbia, MD, USA
[d] Skidmore College, Saratoga Springs, NY, USA
[e] Illinois Fire Service Institute, University of Illinois at Urbana-Champaign, IL, USA
[f] Division of Laboratory Services, National Center for Environmental Health, CDC, Atlanta, GA, USA

A R T I C L E I N F O

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A B S T R A C T

Firefighters may encounter items containing flame retardants (FRs), including organophosphate flame retardants (OPFRs) and polybrominated diphenyl ethers (PBDEs), during structure fires. This study utilized biological monitoring to characterize FR exposures in 36 firefighters assigned to interior, exterior, and overhaul job assignments, before and after responding to controlled residential fire scenarios. Firefighters provided four urine samples (pre-fire and 3-h, 6-h, and 12-h post-fire) and two serum samples (pre-fire and approximately 23-h post-fire). Urine samples were analyzed for OPFR metabolites, while serum samples were analyzed for PBDEs, brominated and chlorinated furans, and chlorinated dioxins. Urinary concentrations of diphenyl phosphate (DPhP), a metabolite of triphenyl phosphate (TPhP), bis(1,3-dichloro-2-propyl) phosphate (BDCPP), a metabolite of tris(1,3-dichloro-2-propyl) phosphate (TDCPP), and bis(2-chloroethyl) phosphate (BCEtP), a metabolite of tris (2-chloroethyl) phosphate (TCEP), increased from pre-fire to 3-hr and 6-hr post-fire collection, but only the DPhP increase was statistically significant at a 0.05 level. The 3-hr and 6-hr post-fire concentrations of DPhP and BDCPP, as well as the pre-fire concentration of BDCPP, were statistically significantly higher than general population levels. BDCPP pre-fire concentrations were statistically significantly higher in firefighters who previously participated in a scenario (within the past 12 days) than those who were responding to their first scenario as part of the study. Similarly, firefighters previously assigned to interior job assignments had higher pre-fire concentrations of BDCPP than those previously assigned to exterior job assignments. Pre-fire serum concentrations of 2,3,4,7,8-pentachlorodibenzofuran (23478-PeCDF), a known human carcinogen, were also statistically significantly above the general population levels. Of the PBDEs quantified, only decabromodiphenyl ether (BDE-209) pre- and post-fire serum concentrations were statistically significantly higher than the general population. These results suggest firefighters absorbed certain FRs while responding to fire scenarios.

1. Introduction

Firefighters' exposures to flame retardants (FRs) including polybrominated diphenyl ethers (PBDEs), non-PBDE brominated flame retardants (NPBFRs), organophosphate flame retardants (OPFRs), and brominated and chlorinated dioxins and furans have increasingly become a topic of concern. PBDEs have been in use since the 1970s, are environmentally persistent, and can remain structurally unchanged on surfaces for long periods of time (e.g., years) (Alexander and Baxter, 2016; Easter et al., 2016). The increased interest in firefighters' exposures to FRs can largely be attributed to their presence in modern home furnishings (e.g., upholstered furniture, carpet padding, electronics),

* Corresponding author. Division of Field Studies and Engineering, National Institute for Occupational Safety and Health, 1090 Tusculum Ave, MS R-14 Cincinnati, OH, 45226, USA.
E-mail address: Nru1@cdc.gov (A.C. Mayer).

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accumulation in humans, and association with adverse health effects (Herbstman et al., 2010; Linares et al., 2015).

Studies that have indicated an elevated risk of cancer for firefighters (Daniels et al., 2014; Jalilian et al., 2019; Lee et al., 2020; Pinkerton et al., 2020), the International Agency for Research on Cancer (IARC) designation of firefighting as a Group 2B possible human carcinogen (International Agency for Research on Cancer (IARC), 2010), and the complex mixture of combustion byproducts (e.g., polycyclic aromatic hydrocarbons (PAHs), formaldehyde, benzene, FRs) firefighters can be exposed to on the fireground have further raised concerns. IARC has not classified the potential carcinogenicity of PBDEs in humans to date. However, the National Toxicology Program (NTP) found evidence of PBDE carcinogenicity in rodent studies (National Toxicology Program , 2016). Other compounds firefighters are exposed to include dioxins, 2,3,7,8-tetrachlorodibenzo-para-dioxin (2378-TeCDD) and 2,3,4,7,8-pentachlorodibenzofuran (23478-PeCDF), which have been classified by IARC as Group 1 known human carcinogens, and a variety of other combustion byproducts that are known, probable, or possible human carcinogens (International Agency for Research on Cancer (IARC), 2010).

Over the past 10 years, the usage of penta-, octa-, and deca-PBDEs has been restricted globally by the Stockholm Convention (United Nations Environment, 2017). The use of organophosphate flame retardants (OPFRs) in furniture and other household items has increased as a result of PBDE's usage restriction following the classification of this compound class as a persistent organic pollutant (POPs) (Dishaw et al., 2011; National Institute of Environmental Health Sciences (NIEHS), 2018). The potential toxic effects of OPFRs are not fully understood. However, two OPFRs, tris(1,3-dichloro-2-propyl) phosphate (TDCPP) and tris (2-chloroethyl) phosphate (TCEP), are listed in California Prop 65 as potentially carcinogenic (Environmental Protection Agency (EPA)U.S.E.P.A. and Cooke, 2017). Tris(1-chloro-2-propyl) phosphate (TCPP) has been found to be toxic to human cells at high concentrations (An et al., 2016), while triphenyl phosphate (TPhP or TPP) has been found to negatively affect development in zebrafish, mice, and rats (Du et al., 2016; Patisaul et al., 2013; Wang et al., 2018).

Studies have found a variety of FRs, dioxins, and furans on firefighter personal protective equipment (PPE) (Alexander and Baxter, 2016; Easter et al., 2016; Fent et al., 2020b; Mayer et al., 2019) and in air samples taken from a residential room-and-contents fire environment (Fent et al., 2020b). In addition, dust collected from fire stations has been found to contain higher FR levels (e.g., BDE-209 and TDCPP) than other occupational settings (Shen et al., 2015). A more recent study in Canada found fire station dust has high levels of BDE-209 (Gill et al., 2020). These studies suggest that firefighters have the potential to be exposed to these compounds while at the scene of a fire and may also bring the contamination back to their stations.

Biomonitoring and exposure assessment studies have also detected FRs in specimens collected from firefighters. Specifically, a study conducted by Shaw et al. reported elevated concentrations of PBDEs in firefighters' serum compared to the general population (Shaw et al., 2013). Park et al. (2015) reported similar findings, including relatively high serum levels of decabromodiphenyl ether (BDE-209) (Park et al., 2015). Another study reported higher levels of organophosphate flame retardants (OPFRs) metabolites in a sampling of firefighters' urine compared with the general population (Jayatilaka et al., 2017). In part because of these studies, a recent systematic review on occupational exposure to FRs listed firefighters as a workforce warranting further investigation (Gravel et al., 2019).

Exposure to combustion byproducts such as polycyclic aromatic hydrocarbons (PAHs) is also thought to be dependent on the job assignment for firefighters. Previous studies have reported that firefighters assigned to interior response activities (e.g., fire suppression or search and rescue) had higher biological levels of PAH metabolites compared to other job assignments (e.g., outside ventilation, incident command, pump operations, overhaul) on the fireground (Fent et al., 2020a). It is reasonable to assume that FR exposure may follow a similar pattern.

The purpose of this study was to characterize the biological levels of OPFR metabolites (in urine), and PBDEs, brominated and chlorinated furans, and chlorinated dioxins (in serum) in firefighters responding to controlled residential fire scenarios with modern home furnishings (containing FRs). This study design also allowed us to compare how exposures vary over time for firefighters assigned to different job assignments.

2. Methods

2.1. Study design

The study design is described in detail elsewhere (Fent et al., 2020b; Horn et al., 2018). Briefly, over a period of 2 weeks in the summer of 2015, 12 fires were ignited in a 111 m^2 wood-frame residential structure with gypsum board wall/ceiling linings and typical residential furnishings, containing a variety of FRs, including OPFRs, NPBFRs, and PBDEs (as reported in Fent et al., 2020b). 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 re-bonded polyurethane foam padding and new polyester carpet. Floor coverings in the fire rooms and nearby hallway were replaced after each fire. A fire was ignited and allowed to grow until the rooms approached flash-over conditions and became ventilation limited (typically 4–5 min) and then the firefighters were dispatched by apparatus from a nearby staging area and arrived on scene within 1 min. After each fire, the drywall and furniture were replaced. Study results reported here were collected from firefighters prior to and after three of the 12 fires.

A crew of twelve firefighters was paired up by job assignment to carry out a coordinated fireground response to a controlled residential fire, which was repeated the next day using a different fire suppression tactic. Approximately one to two weeks later, the returning firefighters were reassigned to new positions and repeated this experiment. This was done on a total of three crews (12 firefighters per crew, 4 burns per crew). Five firefighters dropped out of the study and were unable to return a week later and were replaced with new participants (resulting in a total of 41 participants). However, urine and serum specimens analyzed for FRs, dioxins and furans were only collected from one of the four fires for 36 firefighters. Crew A previously responded to a fire scenario as part of this study seven days prior to the fire where specimens were collected; Crew B responded to a fire scenario twelve days prior to the fire where specimens were collected; and Crew C provided specimens on the first fire they responded to as part of this study. The variability for each crew's recent fire exposure as part of this study allowed us to compare how time since last exposure impacted FR, dioxin, and furan urinary and serum concentrations. More information on the timing of the fire scenarios relative to the specimen collections is provided in Fig. 1. All firefighters participating in the fire scenarios wore a full PPE ensemble that included a protective hood, gloves, turnout gear, and self-contained breath apparatus (SCBA). Each firefighter was provided brand new turnout jackets, hoods, and gloves prior to the first scenario. Relevant demographic information for participating firefighters is provided in Table 1. Tobacco use was an exclusion criteria for this study.

Firefighters were assigned to one of three groups for each scenario. Firefighters assigned to interior response either pulled a primary hoseline and suppressed all active fire or entered the structure and searched for and rescued two simulated occupants (75 kg mannequins). Firefighters assigned to exterior response created openings in the windows and roof to ventilate the structure and/or completed typical exterior operations on the fireground (incident command (IC), pump operation). Importantly, these firefighters never entered the structure. Firefighters assigned to overhaul were outside the structure during active fire, either holding a secondary line or as a rapid intervention team (RIT). After the

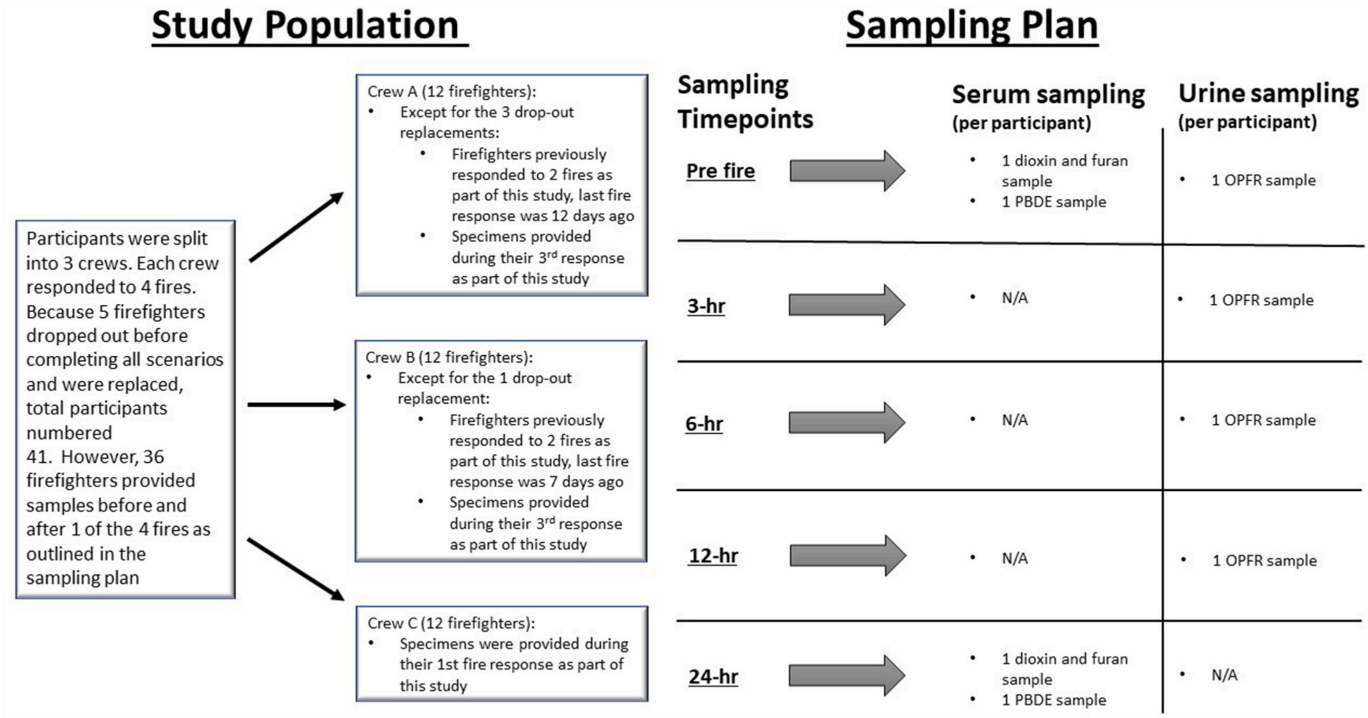

Fig. 1. Study population and sampling strategy for controlled residential fire responses with furnishings containing flame retardants.

Table 1
Characteristics of study participants.

Characteristic	Frequency
Sex	
Male (%)	32 (89)
Female (%)	4 (11)
Age	
Median (Range)	36 (21–52)
BMI	
Median (Range)	26.9 (20.5–34.2)
Home State	
Illinois (%)	22 (61)
Georgia (%)	4 (11)
Indiana (%)	4 (11)
South Dakota (%)	3 (8.3)
Wisconsin (%)	2 (5.5)
Ohio (%)	1 (2.8)

fire was suppressed by the interior firefighters, 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 firefighters walked to an open bay (approximately 40 m from the structure) where PPE was removed, turnout jackets hung in individual lockers and firefighting gloves placed on a shelf. Firefighters used skin cleansing wipes immediately post-fire and showered within an hour after the scenario. After doffing their gear, firefighters entered an adjacent bay where they provided biological samples. Firefighters provided a spot urine sample prior to the scenario (pre-fire) and 3 subsequent spot urine samples after the scenario (3-h, 6-h, 12-h post-fire). Firefighters also provided one serum sample prior to the fire (pre-fire serum) and one serum sample approximately 23 h after the scenario (post-fire serum).

2.2. Urine sampling

Prior to urine collection, participants were instructed to thoroughly rinse hands with water only and air dry their hands, avoiding the use of paper towels. Participants were also instructed to avoid touching the internal surface of the urine cup or the lid to avoid contaminating the sample. Participants were asked to provide a minimum 60 mL of urine for each void. Urine was put on ice and within 4 h, aliquoted into multiple tubes for analyses including 5 mL and 2 mL polypropylene vials for FR and creatinine quantification, respectively and then frozen at −20 °C. The samples were then shipped to the lab on dry ice and stored frozen until analysis.

2.3. Blood sampling

Blood was collected in multiple collecting tubes including two red top 10 mL glass blood collection tubes, and the samples were placed in a rack to clot for 2 h at room temperature. Blood samples were then centrifuged for 15 min at 1000-1300×*g*. Investigators pipetted serum from each participant's red-top tubes into separate 10 mL amber glass jars, one for PBDEs and serum lipids and one for dioxins and furans, and then froze the samples at −20 °C The samples were then shipped to the lab on dry ice and stored frozen until analysis.

2.4. Sample analyses

Urine samples (N = 144) were analyzed for eight OPFR metabolites and one NPBFR metabolite at the Centers for Disease Control and Prevention (CDC) as described by Jayatilaka et al. (2017) (Table 2). The OPFR metabolites measured were: diphenyl phosphate (DPhP), bis(1, 3-dichloro-2-propyl) phosphate (BDCPP), bis(1-chloro-2-propyl) phosphate (BCPP), bis(2-chloroethyl) phosphate (BCEtP), di-p-cresylphosphate (DpCP), di-o-cresylphosphate (DoCP), dibutyl phosphate (DBuP), and dibenzyl-phosphate (DBzP); the NPBFR was 2,3, 4,5-tetrabromobenzoic acid (TBBA). Specific gravity was measured in the field with a handheld refractometer (Atago, Uricon-Ne Product numbers 2722. Reading range 1.000–1.050 UG). Creatinine was measured at CDC using an enzymatic method with a Roche/Hitachi Cobas® c501 chemical analyzer (Roche Diagnostics, Inc., Indianapolis, IN). After enzymatic hydrolysis of 400-μL urine samples and off-line

Table 2
Flame retardant, dioxin, and furan biomarkers quantified in urine and serum.

Type of sample	Parent Chemical	Biomarker
Organophosphate Flame Retardants (OPFRs)		
Urinary	Triphenyl phosphate (TPP or TPhP), Isopropylphenyl diphenyl phosphate t-Butylphenyl diphenyl phosphate 2-Ethylhexyl diphenyl phosphate	Diphenyl phosphate (DPhP)
	Tris(1,3-dichloro-2-propyl) phosphate (TDCPP)	Bis(1,3-dichloro-2-propyl) phosphate (BDCPP)
	Tri-p-cresyl phosphate (TpCP)	Di-p-cresyl phosphate (DpCP)
	Tris(1-chloro-2-propyl) phosphate (TCPP or TCIPP)	Bis(1-chloro-2-propyl) phosphate (BCPP)
	Tributyl phosphate (TBP or TBuP)	Dibutyl phosphate (DBP or DBuP)
	Tribenzyl phosphate (TBzP)	Dibenzyl phosphate (DBzP)
	Tris(2-chloroethyl) phosphate (TCEP)	Bis(2-chloroethyl) phosphate (BCEtP)
	Tri-o-cresyl phosphate (ToCP)	Di-o-cresyl phosphate (DoCP)
	Non-PBDE-brominated flame retardants (NPBFRs)	
	2-Ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB)	2,3,4,5-Tetrabromobenzoic acid (TBBA)
Polybromianted Diphenyl Ethers (PBDEs)		
Serum	2,2′,4-tribromodiphenyl ether (BDE-17)	BDE-17
	2,4,4′-tribromodiphenyl ether (BDE-28)	BDE-28
	2,2′,4,4′-tetrabromodiphenyl ether (BDE-47)	BDE-47
	2,3′,4,4′-tetrabromodiphenyl ether (BDE-66)	BDE-66
	2,2′,3,4,4′-pentabromodiphenyl ether (BDE-85)	BDE-85
	2,2′,4,4′,5-pentabromodiphenyl ether (BDE-99)	BDE-99
	2,2′,4,4′,6-pentabromodiphenyl ether (BDE-100)	BDE-100
	2,2′,4,4′,5,5′-hexabromodiphenyl ether (BDE-153	BDE-153
	2,2′,4,4′,5,6′-hexabromodiphenyl ether (BDE-154)	BDE-154
	2,2′,3,4,4′,5′,6-heptabromodiphenyl ether (BDE-183)	BDE-183
	2,2′,3,3′,4,4′,5,5′,6-nonabromodiphenyl ether (BDE-206)	BDE-206
	decabromodiphenyl ether (BDE-209)	BDE-209
	Brominated furans	
	2,3,7,8-tetrabromodibenzofuran (2378-TeBDF)	2378-TeBDF
	2,3,4,7,8-pentabromodibenzofuran (23478-PeBDF)	23478-PeBDF
	1,2,3,4,7,8-hexabromodibenzofuran (123478-HxBDF)	123478-HxBDF
	Chlorinated dioxins	
	2,3,7,8-Tetrachlorodibenzodioxin (2378-TeCDD)	2378-TeCDD
	1,2,3,7,8-Pentachlorodibenzodioxin (12378-PeCDD)	12378-PeCDD
	1,2,3,4,7,8-Hexachlorodibenzodioxin (123478-HxCDD)	123478-HxCDD
	1,2,3,6,7,8-Hexachlorodibenzodioxin (123678-HxCDD)	123678-HxCDD
	1,2,3,7,8,9-Hexachlorodibenzodioxin (123789-HxCDD)	123789-HxCDD
	1234678-HpCDD	1234678-HpCDD
	Octachlorodibenzodioxin (OcCDD)	OcCDD
	Chlorinated furans	
	2,3,7,8-Tetrachlorodibenzofuran (2378-TeCDF)	2378-TeCDF
	1,2,3,7,8-Pentachlorodibenzofuran (12378-PeCDF)	12378-PeCDF
	(2,3,4,7,8-Pentachlorodibenzofuran) 23478-PeCDF	23478-PeCDF
	1,2,3,4,7,8-Hexachlorodibenzofuran (123478-HxCDF)	123478-HxCDF
	1,2,3,6,7,8-Hexachlorodibenzofuran (123678-HxCDF)	123678-HxCDF
	123789-HxCDF	123789-HxCDF
	2,3,4,6,7,8-Hexachlorodibenzofuran (234678-HxCDF)	234678-HxCDF
	1,2,3,4,6,7,8-Heptachlorodibenzofuran (1234678-HpCDF)	1234678-HpCDF
	1,2,3,4,7,8,9-Heptachlorodibenzofuran (1234789-HpCDF)	1234789-HpCDF
	Octachlorodibenzofuran (OcCDF)	OcCDF

solid phase extraction, target OPFR and NPBFR metabolites were separated via reversed phase high-performance liquid chromatography, and detected by isotope dilution-electrospray ionization tandem mass spectrometry.

Serum samples collected from firefighters were analyzed at CDC for a panel of PBDEs, brominated and chlorinated dioxins and furans performed by gas chromatography isotope dilution high resolution mass spectrometry (GC-IDHRMS) employing a DFS (Thermo DFS, Bremen, Germany) instrument, as previously detailed (Jones et al., 2012).

2.5. Data analysis

Descriptive statistics were displayed as frequency (%), mean ± standard deviation (SD), median, and range for firefighter characteristics. Number of samples, number of samples with concentrations below the limit of detection (LOD), geometric mean (GM), and geometric standard deviation (GSD) were provided for urine and serum concentrations by job assignment and by exposure time. LOD divided by square root of two was assigned to non-detectable concentrations (Hornung and Reed, 1990). Urinary concentrations were adjusted for creatinine (Boeniger et al., 1993).

A Welch's *t*-test or unequal variances *t*-test was used to determine concentration differences for all analytes between the U.S. general population aged 18 years and older and firefighters by job assignment and exposure time. The comparisons were also applied to each sex. A paired *t*-test was utilized to examine whether the change in serum concentrations from pre to post-fire was significantly different from zero. Concentrations for urinary and blood samples were log transformed because corresponding distributions were skewed to the right. For urinary samples, a mixed model with individual firefighter as a random effect was utilized to account for the statistical correlation among exposure time from the same firefighter. The model incorporated the use of maximum likelihood estimation method to reduce bias resulting from the data with non-detectable or left-censored concentrations (Jin et al., 2011). Univariable analyses of longitudinal urinary data were carried out using the log-transformed concentration as the dependent variable. Covariates treated as fixed effects, including exposure times (pre-fire, 3-h post, 6-h post, and 12-h post) and job assignments (exterior, interior, and overhaul), were evaluated. With respect to urine samples, an analysis of covariance (ANCOVA) was used to examine whether the means of a dependent variable, post urine concentration, were equal across job assignments, while statistically controlling for the effect of pre urine concentration. Statistical tests were two-sided at the 0.05 significance level. All analyses were performed in SAS version 9.4 (SAS Institute, Cary, NC).

3. Results

3.1. OPFR urinary results

Urinary concentrations of FRs measured among the majority of firefighters responding in three job assignment classifications during four urine collection times are summarized in Table 3. DPhP, BDCPP, and BCEtP were detected more frequently (detection rate > 60%) than the other metabolites measured in this study. Overall, GM concentrations of DPhP and BDCPP at multiple collection time points were higher than concentrations found in the general population. Specifically, 3-h and 6-h post-fire DPhP GM concentrations for all three job assignments (ranging from 1.38 μg/g creatinine to 1.75 μg/g creatinine) were statistically significantly greater than the GM of the general population (0.80 μg/g creatinine). Additionally, GM concentrations of BDCPP in the three job assignments during the four collection times ranged from 1.86 μg/g creatinine to 3.32 μg/g creatinine and were statistically significantly greater than the GM of general population (0.79 μg/g creatinine). We also stratified by sex and compared DPhP, BDCPP, and BCEtP concentrations with the general population in Supplemental Materials (Table S1). Results for the other urinary biomarkers detected less frequently (<60%) are provided in Supplemental Materials (Table S2).

Results of univariable analyses of repeated measures data with natural logarithm of urinary concentrations as the dependent variable are presented in Table 4. For DPhP and BDCPP, maximum urinary concentrations occurred 3-h post-firefighting, but this increase relative to the pre-fire concentrations was only statistically significant for DPhP (p-value is < 0.001). The mean urinary concentrations of DPhP and BDCPP decreased with each subsequent collection, however the 12-h post-fire DPhP concentrations were still higher than the pre-fire levels (p-value is < 0.05). For BCEtP, maximum urinary concentrations occurred 6-h post-firefighting (p-value is < 0.05 compared to the pre-fire concentrations), but then decreased to levels below the pre-fire concentrations (p-value is < 0.001) 12-h post-fire. There were no statistically significant differences in DPhP, BDCPP, and BCEtP for 3- and 6-h urinary mean concentrations among the three job assignments, adjusting for pre-fire concentrations. However, firefighters assigned to overhaul had statistically significantly higher 6-h BDCPP concentrations compared to those assigned to interior response in this analysis despite the requirement that firefighters wore SCBA during overhaul response.

Univariable results using pre-fire urinary concentrations as the dependent variable are provided in Table 5. Pre-fire BDCPP urinary concentrations were statistically significantly higher for firefighters who previously worked a scenario 7 days ago compared to those who were responding to their first scenario as part of this study (p-value is < 0.05). When comparing firefighters who last participated in a fire scenario 7 days and 10 or more days ago, firefighters who participated 10 days or more ago had statistically significantly lower BDCPP concentrations by comparison (p-value is < 0.05). When examining the job assignment for the previous scenario, firefighters who were previously assigned to interior response had statistically significantly higher pre-fire BDCPP concentrations than firefighters previously assigned to exterior response (p-value is 0.030).

Table 3
Firefighter urine biomarker concentrations[A] (μg/g creatinine) by job assignment compared to the general population (GP).

		Pre-fire Concentration			3-Hour Post-fire Concentration			6-Hour Post-fire Concentration			12-Hour Post-fire Concentration		
Biomarker	Job Assignment	N (N < LOD[B])	GM (GSD)	P-value (vs. GP)	N (N < LOD[B])	GM (GSD)	P-value (vs. GP)	N (N < LOD[B])	GM (GSD)	P-value (vs. GP)	N (N < LOD[B])	GM (GSD)	P-value (vs. GP)
DPhP	**All Firefighters**	36 (3)	0.97 (1.98)	0.103	36 (3)	1.67 (1.94)	**<0.001**[E]	36 (0)	1.58 (1.96)	**<0.001**[E]	36 (1)	1.20 (2.13)	**0.003**[E]
	Exterior	12 (2)	0.95 (2.37)	0.489	12 (1)	1.55 (2.05)	**0.009**[E]	12 (0)	1.38 (2.15)	**0.032**[E]	12 (0)	1.22 (2.18)	0.088
	Interior	12 (1)	1.04 (1.92)	0.196	12 (1)	1.72 (2.11)	**0.005**[E]	12 (0)	1.66 (2.31)	**0.012**[E]	12 (0)	1.28 (2.53)	0.105
	Overhaul	12 (0)	0.92 (1.74)	0.403	12 (1)	1.75 (1.75)	**<0.001**[E]	12 (0)	1.72 (1.43)	**<0.001**[E]	12 (1)	1.10 (1.78)	0.080
	General Population[C]	1901 (187)	0.80 (2.59)	Reference	**	**	Reference	**	**	Reference	**	**	Reference
BDCPP	**All Firefighters**	36 (0)	2.38 (2.12)	**<0.001**[E]	36 (0)	2.70 (1.97)	**<0.001**[E]	36 (0)	2.57 (2.01)	**<0.001**[E]	36 (0)	2.13 (1.99)	**0 < .001**[E]
	Exterior	12 (0)	2.73 (2.22)	**<0.001**[E]	12 (0)	3.32 (2.11)	**<0.001**[E]	12 (0)	2.63 (2.07)	**<0.001**[E]	12 (0)	2.23 (1.97)	**0 < .001**[E]
	Interior	12 (0)	2.09 (2.10)	**0.003**[E]	12 (0)	2.25 (1.83)	**<0.001**[E]	12 (0)	2.07 (1.98)	**<0.001**[E]	12 (0)	1.86 (2.06)	**0.002**[E]
	Overhaul	12 (0)	2.38 (2.13)	**<0.001**[E]	12 (0)	2.64 (1.95)	**<0.001**[E]	12 (0)	3.11 (1.96)	**<0.001**[E]	12 (0)	2.33 (2.01)	**0 < .001**[E]
	General Population[C]	1886 (174)	0.79 (2.83)	Reference	**	**	Reference	**	**	Reference	**	**	Reference
BCEtP	**All Firefighters**	36 (6)	0.28 (3.01)	**0.048**[D]	36 (8)	0.34 (2.09)	0.117	36 (1)	0.36 (1.83)	0.170	36 (5)	0.20 (2.03)	**<0.001**[D]
	Exterior	12 (2)	0.47 (2.43)	0.630	12 (2)	0.38 (1.94)	0.701	12 (1)	0.37 (1.75)	0.538	12 (2)	0.23 (1.81)	**0.005**[D]
	Interior	12 (3)	0.24 (2.92)	0.119	12 (4)	0.33 (2.10)	0.302	12 (0)	0.33 (1.78)	0.195	12 (1)	0.17 (2.51)	**0.006**[D]
	Overhaul	12 (1)	0.20 (3.37)	0.058	12 (2)	0.31 (2.34)	0.256	12 (0)	0.37 (2.02)	0.641	12 (2)	0.21 (1.82)	**0.002**[D]
	General Population[C]	1897 (240)	0.41 (3.10)	Reference	**	**	Reference	**	**[Ga]	Reference	**	**	Reference

A. Metabolites with less than 60% detection rate are summarized in Supplemental Materials (Table S2).
B. Limit of detection (LOD) for each analyte in μg/L: DPhP = 0.16, BDCPP = 0.11, BCEtP = 0.08.
C. Ospina, M., Jayatilaka, N., Wong, L.-Y., Restrepo, P., Calafat AM., 2018 Exposure to organophosphate flame retardant chemicals in the U.S. general population: Data from the 2013–2014 National Health and Nutrition Examination Survey. *Environmental International*. 110, 32–41. Participants aged 18 and older are included.
D. Results were significantly lower than the general population.
E. Results were significantly higher than the general population.
** GM and GSD of general population were listed in the pre-fire columns.

Table 4
Univariable analysis using urine metabolite concentrationsA (μg/g creatinine) as the dependent variable.

Outcome	Logarithm of DPhP Concentration			Logarithm of BDCPP Concentration			Logarithm of BCEtP Concentration		
Covariate	Estimate (SE)	Factor	P-value	Estimate (SE)	Factor	P-value	Estimate (SE)	Factor	P-value
Exposure Time									
Pre-Fire	Reference			Reference			Reference		
3-Hour Post	0.54 (0.10)	1.72	**<0.001**	0.13 (0.08)	1.13	0.141	0.15 (0.12)	1.16	0.243
6-Hour Post	0.52 (0.10)	1.68	**<0.001**	0.08 (0.08)	1.08	0.374	0.31 (0.12)	1.37	**0.013**
12-Hour Post	0.23 (0.10)	1.26	**0.022**	−0.11 (0.08)	0.89	0.191	−0.34 (0.12)	0.71	**0.009**
3-Hour Post	Reference			Reference			Reference		
6-Hour Post	−0.03 (0.10)	0.97	0.792	−0.05 (0.08)	0.95	0.548	0.17 (0.12)	1.18	0.176
12-Hour Post	−0.31 (0.10)	0.73	**0.003**	−0.24 (0.08)	0.79	**0.007**	−0.48 (0.12)	0.62	**<0.001**
6-Hour Post	Reference			Reference			Reference		
12-Hour Post	−0.28 (0.10)	0.75	**0.006**	−0.19 (0.08)	0.83	**0.032**	−0.65 (0.12)	0.52	**<0.001**
Outcome	**Logarithm of 3-Hour Post DPhP Concentration**			**Logarithm of 3-Hour Post BDCPP Concentration**			**Logarithm of 3-Hour Post BCEtP Concentration**		
Covariate[B]	**Estimate (SE)**	**Factor**	**P-value**	**Estimate (SE)**	**Factor**	**P-value**	**Estimate (SE)**	**Factor**	**P-value**
Job Assignment									
Exterior	Reference			Reference			Reference		
Interior	0.05 (0.21)	1.05	0.812	−0.22 (0.20)	0.80	0.284	0.23 (0.18)	1.26	0.213
Overhaul	0.15 (0.21)	1.16	0.491	−0.14 (0.20)	0.87	0.480	0.29 (0.18)	1.34	0.119
Interior	Reference			Reference			Reference		
Overhaul	0.10 (0.21)	1.10	0.652	0.08 (0.20)	1.08	0.703	0.06 (0.17)	1.07	0.705
Outcome	**Logarithm of 6-Hour Post DPhP Concentration**			**Logarithm of 6-Hour Post BDCPP Concentration**			**Logarithm of 6-Hour Post BCEtP Concentration**		
Covariate[B]	**Estimate (SE)**	**Factor**	**P-value**	**Estimate (SE)**	**Factor**	**P-value**	**Estimate (SE)**	**Factor**	**P-value**
Job Assignment									
Exterior	Reference			Reference			Reference		
Interior	0.13 (0.21)	1.14	0.536	−0.03 (0.15)	0.97	0.820	0.13 (0.20)	1.13	0.524
Overhaul	0.25 (0.21)	1.28	0.237	0.27 (0.15)	1.31	0.077	0.35 (0.20)	1.41	0.095
Interior	Reference			Reference			Reference		
Overhaul	0.12 (0.21)	1.13	0.567	0.31 (0.15)	1.36	**0.048**	0.22 (0.19)	1.25	0.258

A. No univariable analysis was conducted for metabolites with less than 60% detection rates (BCPP, DBuP, DpCP, TBBA, DoCP, and DBzP).
B. Logarithm of pre-fire concentration was adjusted for in the model.

3.2. PBDE and brominated and chlorinated dioxin and furan serum results

The levels of the PBDEs which were detected most frequently (>60%) in serum samples are summarized in Table 6. Six compounds (BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, and BDE-209) were detected in more than 60% of the samples. Several of these compounds were below the levels reported in the general population, and no analytes significantly increased from pre- to post-fire. Concentrations for these six compounds were also stratified by sex and compared to the general population in Supplemental Materials (Table S3) The remaining PBDEs are summarized in Supplemental Materials (Table S4).

Although the change from pre- to post-fire was not statistically significant, BDE-209 was detected more frequently and had statistically significantly greater GM concentrations (2.91 and 3.01 ng/g lipid for pre- and post-fire serum samples) than the general population (1.89 ng/g lipid; p-values < 0.001). Pre- and post-fire serum GM concentrations of BDE-209 in the overhaul group (3.82 and 3.53 ng/g lipid, respectively) were also statistically significantly greater than the general population (p-values < 0.001), while firefighters assigned to exterior and interior response had higher post-fire serum GM concentrations (2.69 and 2.86 ng/g lipid, correspondingly) compared to the general population (respective p-values <0.05). Pre-fire serum BDE-209 concentrations were also used as the dependent variable to see how previous job assignment or days since last assignment impacted exposures, but results were similar and not statistically significant (data not shown).

Firefighters also provided serum samples that were pooled by job assignment groupings and analyzed for brominated and chlorinated furans and chlorinated dioxins, summarized in Supplemental Materials (Table S5). Compared to the brominated furans, chlorinated dioxins and furans were detected more frequently in the serum. Firefighters were found to have statistically significantly higher pre-fire GM serum concentrations of 23478-PeCDF, and pre- and post-fire GM serum concentrations of 1,2,3,4,7,8-Hexachlorodibenzofuran (123478-HxCDF), 1,2,3,6,7,8-Hexachlorodibenzofuran (123678-HxCDF), and 2,3,4,6,7,8-Hexachlorodibenzofuran (234678-HxCDF) than the general population. Job assignment did not appear to have a strong effect on the serum concentrations. The few statistically significant findings by job assignment appeared to be related to the precision in the measurements (GSD) rather than the magnitude of the differences. Additionally, there were no statistically significant increases in serum concentrations from pre to post-fire.

4. Discussion

This study was designed to simulate a fire environment where firefighters responded to realistic scenarios and were assigned to common job assignments including interior, exterior and overhaul response. The fire environment included common home furnishings containing FRs. Specifically, this study characterized firefighters' exposure to FRs during common job assignments through urinary and serum samples.

We measured statistically significantly higher concentrations of BDCPP and DPhP in firefighters' urine post-fire compared to the general population. Interestingly, firefighters' pre-fire BDCPP concentrations were also statistically significantly higher than the general population, which was not true for DPhP or BCEtP. Additionally, we found DPhP concentrations in samples taken post-fire (3-h, 6-h, 12-h) were statistically significantly higher than pre-fire samples. The fact that BDCPP and DPhP are the most abundant OPFR urinary metabolites measured in this study is consistent with our previous environmental monitoring results (Fent et al., 2020b). Median air concentrations of TPhP (the parent compound of DPhP) were 3000-fold higher than any other OPFRs

Table 5
Univariable analysis using pre-fire urine metabolite concentrations[A] (μg/g creatinine) as the dependent variable.

Outcome	Logarithm of Pre DPhP Concentration			Logarithm of Pre BDCPP Concentration		
Covariate	Estimate (SE)	Factor	P-value	Estimate (SE)	Factor	P-value
Days Since Last Fire Scenario (Categorical)						
NA (N = 16)	Reference			Reference		
7 Days (N = 11)	−0.31 (0.27)	0.73	0.259	0.58 (0.28)	1.78	**0.045**
10 (N = 1) and 12 (N = 8)	−0.15 (0.29)	0.86	0.610	−0.20 (0.29)	0.82	0.508
7 Days	Reference			Reference		
10 and 12 Days	0.16 (0.31)	1.18	0.604	−0.77 (0.32)	0.46	**0.021**
Pre-Fire Group						
NA	Reference			Reference		
Exterior	−0.17 (0.34)	0.85	0.633	−0.31 (0.37)	0.73	0.409
Interior	0.04 (0.29)	1.04	0.899	0.62 (0.31)	1.86	0.055
Overhaul	−0.60 (0.30)	0.55	0.055	0.16 (0.33)	1.17	0.628
Exterior	Reference			Reference		
Interior	0.20 (0.38)	1.22	0.599	0.93 (0.41)	2.54	**0.030**
Overhaul	−0.44 (0.39)	0.65	0.273	0.47 (0.42)	1.60	0.275
Interior	Reference			Reference		
Overhaul	−0.64 (0.35)	0.53	0.074	−0.46 (0.37)	0.63	0.224

A. No univariable analysis was conducted for metabolites with less than 60% detection rates (BCPP, DBuP, DpCP, TBBA, DoCP, and DBzP).

analyzed in this study (408 μg/m^3) and TPhP was detected most frequently during overhaul as well. Surface wipe samples were also taken from turnout jackets worn by firefighters responding to these scenarios, and TDCPP (the parent compound of BDCPP) and TPhP were two of the most abundant compounds measured (Fent et al., 2020b). TPhP was also detected in bulk samples taken from headboard padding and chair cushions that were burned in the scenarios, while TDCPP was only detected in carpet padding (Table S6; Fent et al., 2020b). A previous publication found similar urinary results, reporting elevated concentrations of DPhP and BDCPP in firefighters' urine collected at the same training academy (Jayatilaka et al., 2017) where samples were collected for this study.

BCEtP pre-fire concentrations were lower than the general population, but the 6-h post-fire concentrations were statistically significantly increased from the pre-fire concentrations (though not statistically significantly higher than general population levels). Of note, we did not detect TCEP (the parent compound of BCEtP) in air or on turnout gear, although it was found in the bulk sample of carpet liner included in the scenarios (Table S6; Fent et al., 2020b). Nevertheless, the increase in urinary concentrations of BDCPP, DPhP, and BCEtP after firefighting suggest biological uptake of the parent compounds.

We stratified DPhP, BDCPP, and BCEtP urinary concentrations by sex and compared to the general population. Males in this study were more likely than their female counterparts to have concentrations above the male general population, but this is likely due in large part to the small sample size for females (n = 4). We also compared urinary concentrations by job assignment. Firefighters assigned to overhaul had statistically significantly higher 6-h BDCPP concentrations compared to interior firefighters. However, those who were previously assigned to interior response (a week or more prior) had statistically significantly higher pre-fire BDCPP urinary concentrations compared to those previously assigned to exterior or overhaul. Additionally, firefighters who last participated in a scenario 7 days prior had statistically significantly higher pre-fire urinary concentrations of BDCPP compared to those who were participating in their first scenario as part of this study. It is likely that the exposure from the previous scenario contributed to firefighters' elevated pre-fire BDCPP concentrations, particularly for those who were previously assigned to interior response. It is also possible the firefighters were exposed to FRs through their occupation. For example (Shaw et al., 2013), measured higher levels of BDCPP in California firefighters compared to the general population. Unfortunately, we did not survey firefighters in this study to determine whether they had responded to emergency fires in the period before specimen collections. A recent publication estimated BDCPP has an elimination half-life of 54 days (Wang et al., 2020) based on concentrations in human plasma and urine, much longer than previously thought (Carignan et al., 2013). Hence, we cannot rule out that work-related exposures from months ago or non-occupational exposures (e.g., diet or contaminated dust in the home) could contribute to the concentrations measured here.

DPhP urinary concentrations were more likely to increase post-fire (3-h, 6-h, 12-h) from pre-fire levels compared to all other analytes (including BDCPP) measured in this study. While TPhP appears to have slower permeation through the skin than many of the other OPFRs (absorption flux in ng cm^{-2} h^{-1}; TCEP = 10, TDCPP = 0.10, TPhP = 0.093) (Frederiksen et al., 2018), it was measured in air during the fires and after suppression at median concentrations that were several orders of magnitude higher than the other OPFRs (Fent et al., 2020b). DPhP post-fire concentrations were marginally higher for firefighters assigned to interior or overhaul compared to those assigned to exterior response. DPhP has a much shorter estimated half-life of 9.5 days (Wang et al., 2020) than BDCPP, which may explain why the firefighters' pre-fire urinary concentrations were near general population levels regardless of the previous job assignment or how long it had been since they participated in a fire scenario. Though differences are not statistically significant, DPhP concentrations were lower for those previously assigned to overhaul compared to those assigned to interior response. Previous studies have found interior response activities like fire suppression and search and rescue led to higher exposures than exterior response activities or overhaul (Fent et al., 2020a, 2020b). Other studies have also explored TPhP exposure in other industries. Estill et al. (2021) found nail salon technicians had DPhP urinary concentrations lower than the current study, but still higher than the general population, while an older study found aircraft technicians had DPhP concentrations similar to those reported here (Schindler et al., 2014).

BDE-209 was the only PBDE that appeared to be higher than general population levels. However, there was not a statistically significant change in serum concentrations of BDE-209 from pre- to post-fire for all firefighters or for firefighters stratified by job assignment. Thus, although BDE-209 was the most abundant PBDE measured in air (both during overhaul and the fire period) and deposited on turnout jackets and hoods used in this study, there is no evidence of significant uptake of BDE-209 over a 23-h period after firefighting as part of this study. Interestingly, firefighters assigned to overhaul had pre-fire serum concentrations that were higher than the general population, suggesting that they may have been exposed before starting the scenario.

However, when we evaluated the effect of previous job assignment and time since last fire scenario on pre-fire BDE-209 serum concentrations, no statistically significant effects were found. There may be a low-level source of chronic BDE-209 exposure among the firefighters in this study that contributed to the serum levels we measured. Alexander and Baxter (2016) found that BDE-209 was one of the most abundant PBDE contaminants on used gear, while Shen et al. (2015) found high levels of BDE-209 in dust samples taken from firehouses relative to samples taken from other occupational settings. Previous studies have also found BDE-209 serum levels for firefighters that were statistically significantly higher than the general population (Park et al., 2015; Shaw et al., 2013).

Table 6
Firefighter PBDE serum concentrations[A] (ng/g lipid) by job assignment compared to the general population (GP).

		Pre-fire Serum Concentration			Post-fire Serum Concentration			
Analyte	Job assignment	N (No. < LOD[B])	GM (ng/g lipid) (GSD)	P-value (vs GP)	N (No. < LOD[B])	GM (ng/g lipid) (GSD)	P-value (vs GP)	P-value (Pre vs Post)
BDE-28	**All firefighters**	36 (4)	0.53 (2.25)	**0.029[D]**	36 (2)	0.54 (2.15)	**0.027[D]**	0.922
	Exterior	12 (2)	0.43 (1.88)	**0.016[D]**	12 (0)	0.43 (1.81)	**0.011[D]**	0.498
	Interior	12 (2)	0.47 (2.06)	0.065	12 (2)	0.47 (1.87)	**0.039[D]**	0.226
	Overhaul	12 (0)	0.74 (2.69)	0.928	12 (0)	0.77 (2.59)	0.823	0.984
	General Population[C]	1637 (178)	0.72 (1.78)	Reference	**	**	Reference	
BDE-47	**All firefighters**	36 (0)	8.49 (2.59)	**0.008[D]**	36 (0)	8.37 (2.57)	**0.006[D]**	0.869
	Exterior	12 (0)	5.94 (1.88)	**0.001[D]**	12 (0)	5.73 (1.86)	**<0.001[D]**	0.172
	Interior	12 (0)	7.58 (2.28)	**0.038[D]**	12 (0)	7.60 (2.23)	**0.034[D]**	0.447
	Overhaul	12 (0)	13.59 (3.29)	0.955	12 (0)	13.47 (3.25)	0.974	0.921
	General Population[C]	1637 (0)	13.32 (1.89)	Reference	**	**	Reference	
BDE-99	**All firefighters**	36 (0)	1.58 (2.80)	**0.007[D]**	36 (0)	1.49 (2.76)	**0.003[D]**	0.816
	Exterior	12 (0)	1.08 (2.01)	**0.001[D]**	12 (0)	0.95 (2.01)	**<0.001[D]**	0.081
	Interior	12 (0)	1.32 (2.62)	**0.035[D]**	12 (0)	1.31 (2.46)	**0.024[D]**	0.135
	Overhaul	12 (0)	2.76 (3.30)	0.852	12 (0)	2.68 (3.23)	0.918	0.899
	General Population[C]	1637 (0)	2.59 (2.12)	Reference	**	**	Reference	
BDE-100	**All firefighters**	36 (1)	1.58 (2.52)	**<0.001[D]**	36 (0)	1.67 (2.28)	**<0.001[D]**	0.992
	Exterior	12 (0)	1.24 (1.56)	**<0.001[D]**	12 (0)	1.19 (1.52)	**<0.001[D]**	0.091
	Interior	12 (0)	1.60 (2.08)	**0.017[D]**	12 (0)	1.54 (2.10)	**0.014[D]**	0.204
	Overhaul	12 (1)	1.99 (3.91)	0.361	12 (0)	2.52 (2.87)	0.657	0.949
	General Population[C]	1637 (0)	2.90 (1.88)	Reference	**	**	Reference	
BDE-153	**All firefighters**	36 (0)	5.66 (2.42)	**<.001[D]**	36 (0)	5.53 (2.44)	**<0.001[D]**	0.907
	Exterior	12 (0)	4.61 (2.22)	**0.008[D]**	12 (0)	4.45 (2.23)	**0.006[D]**	0.347
	Interior	12 (0)	4.37 (2.05)	**0.003[D]**	12 (0)	4.33 (2.09)	**0.003[D]**	0.962
	Overhaul	12 (0)	9.00 (2.68)	0.769	12 (0)	8.80 (2.72)	0.715	0.790
	General Population[C]	1637 (0)	9.81 (1.93)	Reference	**	**	Reference	
BDE-209	**All firefighters**	36 (2)	2.91 (1.79)	**<0.001[E]**	36 (0)	3.01 (1.57)	**<0.001[E]**	0.687
	Exterior	12 (1)	2.35 (1.71)	0.191	12 (0)	2.69 (1.56)	**0.020[E]**	0.359
	Interior	12 (1)	2.75 (1.87)	0.062	12 (0)	2.86 (1.61)	**0.012[E]**	0.720
	Overhaul	12 (0)	3.82 (1.66)	**<0.001[E]**	12 (0)	3.53 (1.53)	**<0.001[E]**	0.257
	General Population[C]	1637 (27)	1.89 (1.64)	Reference	**	**	Reference	

A. PBDEs with less than 60% detection rate are summarized in Supplemental Materials (S4).
B. LOD: limit of detection. Observations below the LOD were substituted using LOD/square root of 2.
C. The data are from the National Health and Nutrition Examination Survey (NHANES) (2020). 2015–2016 data documentation, codebook, and frequencies. Brominated Flame Retardants (BFRs) - Pooled Samples (BFRPOL_I). Available at https://wwwn.cdc.gov/Nchs/Nhanes/2015-2016/BFRPOL_I.htm. Accessed 12 November 2020.
D. Results were significantly lower than the general population.
E. Results were significantly higher than the general population.
** GM and GSD of general population were listed in the pre serum columns.

Of note, BDE-209 has a half-life of 15 days, while tri- to hexaBDEs have half-lives in the range of one to four years (Sjödin et al., 2020; Thuresson et al., 2006). Hence, serum concentrations of BDE-209 represent relatively recent exposures (i.e., within the last month) while lower brominated congeners serum concentrations represent years of accumulated exposure possibly masking any exposures occurring in the last fire scenario.

While BDE-209 concentrations were above the general population, the other BDEs detected most frequently in this study were statistically significantly lower than the general population. To our knowledge, this is the first study reporting lower BDE levels for firefighters compared to the general population, indicating firefighters' exposure to this class of FRs may be decreasing following their usage restriction.

None of the serum concentrations of dioxins or furans increased from pre- to post-fire. In general, chlorinated furans were more likely to be above general population levels than chlorinated dioxins even before the fires (general population data were not available for brominated furans). Specifically, 23478-PeCDF pre-fire concentrations were statistically significantly above the general population. 23478-PeCDF is a Group 1 known human carcinogen, according to IARC (International Agency for Research on Cancer (IARC), 2010), and thus exposure to this compound should be reduced as much as possible. It should be noted that levels in wipe samples of the firefighters' gloves were below the LOD for 23478-PeCDF (Fent et al., 2020b). However, the analysis of chlorinated furans in wipe samples was qualitative in nature, so caution should be exercised when interpreting these findings.

The types and makeup of furnishings and additive FRs in those furnishings will vary greatly from one structure to another. Hence, while we attempted to create a representative residential fire that could be replicated across all three participant crews, these fires certainly do not represent potential exposures across all structure fires. The FRs that dominated in the environmental and biological samples collected in this study could be more or less prevalent in different structure fires. For example, PBDEs were phased out of production in the United States over the past decade, so furniture that has been manufactured more recently will be less likely to contain these chemicals. Therefore, caution should be exercised in generalizing these findings broadly across the U.S. fire service.

This study has some limitations. Most of the firefighters participating in this study were from the Midwest (i.e., Illinois, Wisconsin, Indiana) so a comparison with NHANES, a nationally representative sample, could overlook geographic differences. However, NHANES is the best comparison group available as regionally representative data for Midwest residents does not exist for these compounds. Although most of the urinary metabolites are specific for the parent compounds, it is important to note that some OPFRs have other metabolites (e.g., hydroxyl triphenyl phosphate for TPhP, 1-hydroxy-2-propyl bis(1-chloro-2-propyl) phosphate for TCPP) not included in this study. Additionally, DPhP is a metabolite for several other compounds including isopropylphenyl diphenyl phosphate, t-butylphenyl diphenyl phosphate, and 2-ethylhexyl diphenyl phosphate (Nishimaki-Mogami et al., 1988; Phillips et al., 2020; Shen et al., 2019). However, the metabolites included in this study are those included in NHANES (Ospina et al., 2018), which allowed comparisons to concentrations found in the general population. We did not restrict firefighters from responding to fires as part of their occupation prior to the scenarios (or during the time period between scenarios) and it is possible participants recently responded to fires as part of their occupation (although this was not documented). Given the extended half-lives (i.e., several days) of several of these chemicals (e.g., DPhP, BDCPP, BDE-209), we cannot rule out the possibility that the firefighters' occupation or other non-occupationally related sources of exposure contributed to their metabolite levels even before the fire scenarios and specimen collections in this study. In fact, the data support that the previous fire-scenario assignment (at least 7 days prior) may have contributed to the pre-fire concentrations of BDCPP for some firefighters. Despite this potential confounder, we found post-fire urinary concentrations for several OPFR metabolites that were higher than pre-fire urinary concentrations. Additionally, the parent compounds (TPhP, TDCPP, BDE-209) of the most abundant metabolites (BDCPP, DPhP, BDE-209) were also the most abundant chemicals detected in air and deposited on turnout gear (as reported previously). BDE-209 concentrations were statistically significantly higher than the general population, suggesting firefighters may be chronically exposed to low levels of this chemical as part of their occupation.

This study provides further evidence that firefighters in full protective turnout gear can biologically absorb compounds that are produced or released during fires. While inhalation exposure is possible for firefighters on the exterior of the structure, interior firefighters wore SCBA throughout the response and overhaul firefighters donned SCBA before entering the structure post suppression. Hence, the dermal route likely played an important role in the absorption of the OPFRs. Participants in this study used commercial skin-cleansing wipes (Essendant baby wipes NICA630FW) and showered shortly after completing the scenarios, which likely removed some of the dermal contamination. While the impact of these measures should be further evaluated, higher biological levels may have been experienced if skin cleansing was delayed, which is often the case during emergency fire responses.

5. Conclusions

Firefighters can be exposed to certain PBDEs, OPFRs, and brominated and chlorinated furans and chlorinated dioxins when responding to structure fires containing modern home furnishings. Several FR biomarkers (BDE-209, DPhP, and BDCPP) were consistently detected in biological specimens at concentrations above the general population levels, and other compounds (23478-PeCDF) were above the general population levels during at least one collection period. Urinary concentrations of DPhP increased significantly from pre- to post-fire, suggesting absorption of the parent compound (TPhP) during the fire response. BCEtP concentrations were not above general population levels but did increase significantly pre- to post-fire. Job assignment appears to play an important role, as those who previously worked interior response had higher pre-fire BDCPP concentrations than those who had previously worked exterior operations. That the previous scenario occurred at least 7 days prior to the specimen collection suggests that BDCPP will remain in the body for several days following exposure. Future work should further investigate how job assignment and control interventions (e.g., routine laundering of turnout gear) impact the biological absorption of FRs during structural firefighting.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijheh.2021.113782.

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