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Persistent organic pollutants including polychlorinated and polybrominated dibenzo-*p*-dioxins and dibenzofurans in firefighters from Northern California

Susan D. Shaw [a,c,*], Michelle L. Berger [a], Jennifer H. Harris [a], Se Hun Yun [b], Qian Wu [b,c], Chunyang Liao [b], Arlene Blum [d], Anthony Stefani [e], Kurunthachalam Kannan [b,c]

[a] Marine Environmental Research Institute, Center for Marine Studies, P.O. Box 1652, Blue Hill, ME 04614, USA
[b] Wadsworth Center, New York State Department of Health, Albany, NY 12201, USA
[c] Department of Environmental Health Sciences, School of Public Health, State University of New York at Albany, P.O. Box 509, Albany, NY 12201-0509, USA
[d] Green Science Policy Institute, University of California, Berkeley, CA 94705, USA
[e] San Francisco Firefighters Cancer Prevention Foundation, 1139 Mission St., San Francisco, CA 94103, USA

HIGHLIGHTS

- First study to measure PBDD/Fs in blood of firefighters.
- Distinctive PBDD/F, PCDD/F, PBDE, PFC congener patterns found in firefighter serum.
- The $TEQ_{PBDD/F}$ was 21 times higher than the $TEQ_{PCDD/F}$ in firefighter serum.
- PBDE profiles in serum indicated continuous occupational exposure to deca-BDE.
- Elevated PFNA levels suggested significant exposure to smoke during firefighting.

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ABSTRACT

Polychlorinated and polybrominated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs and PBDD/Fs) were measured in serum of twelve firefighters sampled after a fire event in San Francisco, California, along with polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), *p,p′*-DDE, hexachlorobenzene (HCB), perfluorinated chemicals (PFCs), bisphenol-A (BPA) and tetrabromobisphenol-A (TBBPA). $TEQ_{PCDD/F}$ concentrations were relatively low (mean 5 pg g^{-1} (lipid weight), lw, range 1–11 pg g^{-1} lw), but concentrations of 1,2,3,4,6,7,8-HpCDD, a congener indicative of exposure during firefighting, were elevated. Tentative WHO_{2005}-TEQs calculated for PBDD/Fs in our samples (mean 104 pg g^{-1} lw, range 0.2–734 pg g^{-1} lw) suggested that PBDD/Fs may contribute substantially to dioxin-like toxicity in individual firefighters. PBDE concentrations were elevated in firefighter serum (mean 135 ng g^{-1} lw, range 48–442 ng g^{-1} lw). PBDE-209, PBDE-47 and PBDE-153 were prevalent congeners; PBDE-209 contributed >50% of the total PBDE concentration in four individuals, implying continuous occupational exposure to deca-BDE. Perfluorooctanesulfonate (PFOS) was the dominant PFC in serum (mean 12 ng ml^{-1} (wet weight), ww, range 3 ng ml^{-1} ww to 59 ng ml^{-1} ww), followed by perfluorooctanoic acid (PFOA) (mean 7 ng ml^{-1} ww, range 2 ng ml^{-1} ww to 12 ng ml^{-1} ww). Concentrations of perfluorononanoic acid (PFNA) (mean 2 ng ml^{-1} ww, range 1–4 ng ml^{-1} ww) were higher than those reported in the high-smoke exposure group of World Trade Center fire responders, suggesting that the California firefighters were exposed to PFNA in smoke during firefighting. Given their elevated rates of cancers, these results illustrate the importance of monitoring halogenated contaminants including PBDD/Fs in firefighters.

1. Introduction

Firefighters may be exposed to a wide range of toxic chemicals both during and while cleaning up after fires, including volatile organic compounds, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), brominated flame retardants (BFRs),

* Corresponding author. Address: Marine Environmental Research Institute, Center for Marine Studies, P.O. Box 1652, Blue Hill, ME 04614, USA. Tel.: +1 207 374 2135; fax: +1 207 374 2931.
E-mail address: sshaw@meriresearch.org (S.D. Shaw).

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metals, and various combustion by-products (Brandt-Rauf et al., 1988; Bolstad-Johnson et al., 2000; Schecter et al., 2002; Edelman et al., 2003). The nature and extent of their exposure is highly variable depending on the number of fires, types of firefighting performed, and personal habits. Of major concern during fires is the potential formation of large amounts of by-products such as chlorinated and brominated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs and PBDD/Fs) (Ebert and Bahadir, 2003; Shaw et al., 2010; UNEP, 2010). Although PCDD/Fs and PBDD/Fs are both produced during combustion, the patterns of congeners depend on the substrates, the temperature, and other catalysts that are present. PCDD/Fs are formed during combustion of organic materials in the presence of chlorine, e.g., polyvinyl chloride, PCBs, and chlorinated pesticides (Bumb et al., 1980; Weber and Kuch, 2003; Blomqvist et al., 2007). PBDD/Fs are formed during fires under uncontrolled combustion conditions in the presence of chemical precursors such as the polybrominated diphenyl ethers (PBDEs) (Ebert and Bahadir, 2003; Kannan et al., 2012; UNEP, 2010). California homes, offices, and public buildings contain high concentrations of PBDEs, owing to the state's unique fire regulation TB117 that has led to high usage of BFRs in furniture, electronics, and many other products (Shaw et al., 2010). Accordingly, high concentrations of PBDEs have been reported in California house dust and in breast milk and serum samples (She et al., 2002; Petreas et al., 2003; Zota et al., 2008). In the presence of high concentrations of bromine-containing materials, it is plausible that large amounts of PBDD/Fs would be released during fire events.

Exposure of firefighters to PCDD/Fs has been investigated following acute fire events including the Staten Island transformer fire (Kelly et al., 2002), the Shelekov fire at a cable manufacturing plant in Siberia (Schecter et al., 2002; Chernyak et al., 2009), and the World Trade Center (WTC) fire in New York City (Edelman et al., 2003; Horii et al., 2010). Occupational exposure to PCDD/Fs has also been reported in firefighters who have responded to multiple fires over years (Hsu et al., 2011; Chernyak et al., 2012). The data suggest that firefighter activity may result in distinctive PCDD/F congener profiles in serum, even when the total concentrations of PCDD/Fs are low (Horii et al., 2010; Hsu et al., 2011; Chernyak et al., 2012).

Whereas most investigations have focused on PCDD/Fs, PBDD/Fs are major contaminants both indoors and in the environment (Hanari et al., 2006; Shaw et al., 2010; Kannan et al., 2012). In industrial countries, PBDD/Fs are released from uncontrolled burning of BFR-containing wastes and the resulting emissions contribute substantially to total dioxin-like toxicity (Gullett et al., 2010; UNEP, 2010). In Japan, PBDFs are the major contributors to dioxin-like toxicity in house dust (Suzuki et al., 2010). In the UK, PBDD/Fs and PCDD/Fs contribute about 30% of the dioxin-like toxicity in food (Rose and Fernandes, 2010). A recent study of Swedish adipose tissue samples indicated that PBDD/Fs may contribute up to 14% of the total dioxin toxic equivalents (TEQs) (Jogsten et al., 2010). Similarly, Kotz et al. (2005) reported that the TEQ of PBDD/Fs may account for up to 12% of the dioxin-like toxicity in human milk.

Large amounts of PBDD/Fs can be produced by thermal processing (extrusion, molding, and recycling) of materials containing PBDEs, and elevated PBDD/F concentrations were reported in blood of German workers at a deca-BDE extrusion and blending plant (Zober et al., 1992). The open burning of electronic-waste containing PBDEs is estimated to release tons of PBDD/Fs and PCDD/Fs into the environment (Zennegg et al., 2009). Ma et al. (2009) reported that $TEQ_{PBDD/F}$ concentrations exceeded the $TEQ_{PCDD/F}$ concentrations in environmental samples from an e-waste recycling facility in China.

PBDD/Fs have toxicities similar to their chlorinated counterparts in human cell lines and mammalian species (Weber and Greim, 1997; Birnbaum et al., 2003; Olsman et al., 2007; Samara et al., 2009). In vitro responses include enzyme induction, antiestrogen activity in human breast cancer cells, and transformation of mouse macrophages into tumor cells (WHO, 1998).

Elevated rates of cancer have been reported in firefighters (Hansen, 1990; IARC, 2010; LeMasters et al., 2006; Kang et al., 2008) including four types that are potentially related to exposure to PCDD/Fs—multiple myeloma, non-Hodgkin's lymphoma, prostate, and testicular cancer. A screening study for bladder cancer incidence in San Francisco firefighters found that retired firefighters are at increased risk for transitional cell carcinoma (Green et al., 2008). Firefighters who responded to the WTC collapse have been found to be at high risk for as many as 15 site-specific cancers (Zeig-Owens et al., 2011).

This pilot study was conducted to characterize exposure to PCDD/Fs, PBDD/Fs and other persistent organic pollutants (POPs) in California firefighters. Congener-specific concentrations of PBDD/Fs, PCDD/Fs, PBDEs, PCBs, and perfluorinated chemicals (PFCs), as well as *p–p′*-DDE, hexachlorobenzene (HCB), tetrabromobisphenol-A (TBBPA) and bisphenol-A (BPA) were analyzed in serum of firefighters sampled after a fire event in San Francisco, California. Dioxin toxic equivalents (TEQs) were calculated for the PCDD/Fs detected in firefighter serum using 2005 World Health Organization (WHO) toxic equivalency factors (TEFs) (Van den Berg et al., 2006). Tentative TEQs were calculated for PBDD/Fs using the WHO_{2005}-TEFs for chlorinated analogs. Examination of contaminant concentrations and congener profiles in serum of California firefighters may provide important information for the subsequent evaluation of health effects.

2. Materials and methods

2.1. Study subjects and serum sample collection

The study subjects were veteran firefighters working at different stations in San Francisco, California, who had been enrolled in a medical monitoring program. Twelve firefighters were recruited for the study by the San Francisco Firefighters Cancer Prevention Foundation in fall 2009 and occupational history data were collected by questionnaire. All twelve firefighters completed the questionnaire. The firefighters were selected according to the following criteria: (1) they had not worked in industries with known chemical emissions; (2) they were firefighters for at least 5 years; and (3) they had responded to fire scenes at least 20 times in the past 5 years. Institutional Review Board approvals were obtained to collect and analyze blood plasma samples. Blood samples were collected within 24 h of responding to a fire. Blood samples were drawn by San Francisco Department of Public Health paramedics at the Ralph Davies Medical Center from the anticubital vein using an 18 gauge needle and chemically clean vacutainer blood tubes that contained no anti-coagulants. Each subject provided 100 mL of venous blood which was kept cool in a refrigerator until it was spun down to approximately 40 mL serum. Serum samples were frozen at −20 °C and shipped frozen overnight (on dry ice) for analysis.

2.2. Chemical analysis

Concentrations of PCDD/Fs, PBDD/Fs, PBDEs, PCBs, *p,p′*-DDE, HCB, PFCs, BPA, and TBBPA were determined in serum by high resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS). ^{13}C labeled PCDD/Fs (EDF-4053, Cambridge Isotope Laboratories, Andover, MA) (2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,4,6,7,8-HpCDD, OCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 1,2,3,6,7,8-HxCDF, and 1,2,3,4,6,7,8-HpCDF) and

PBDD/Fs (EDF-5071, Cambridge Isotope Laboratories, Andover, MA, USA) (1,2,3,7,8-PeBDD, 2,3,7,8-TBDF, 1,2,3,7,8-PeBDF, 2,3,4,7,8-PeBDF, and 1,2,3,4,7,8-HxCDF) were used as internal standards. Concentrations of PFCs, BPA, and TBBPA were determined by high-performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS). $^{13}C_4$ PFOS, $^{13}C_4$ PFOA, $^{13}C_2$ PFNA, $^{13}C_2$ PFDA (Wellington Laboratories, Ontario, Canada) and d_{16}-BPA (Cambridge Isotope Laboratories, Andover, MA, USA) were used as internal standards for isotopic dilution method. Details of the analytic procedures are provided in Supplementary Materials.

2.3. Questionnaire

A written questionnaire was administered to each subject via an interview with a trained member of the board of the San Francisco Firefighters Cancer Prevention Foundation. The questionnaire included a range of questions relating to personal characteristics that may influence exposure to contaminants (age, gender, region of residence), lifestyle (smoking), medical issues, and work history (length of time fighting fires, number of fires per year, job responsibilities, and use of personal protective equipment). Information obtained from the questionnaire was used in the statistical analysis (Table SI-1).

2.4. Statistical analysis

Data were analyzed using the statistical software package SPSS (version 15.0, SPSS, Inc., Chicago, IL) and R v 2.13.1. Concentrations below the limit of detection (LOD) were calculated by treating the result as half the LOD. For compounds detected in <50% of the samples, concentrations below the LOD were assigned a zero value. Questionnaire data was examined to explore factors that may affect chemical concentrations. The Spearman's rank correlation test was applied to identify intercorrelations among the contaminants and between contaminants and demographic variables. Mann–Whitney U tests were conducted to determine how contaminant concentrations varied by demographic groups.

3. Results and discussion

3.1. Study population

Demographic characteristics of the 12 study participants are shown in Table SI-1 (Supplementary Material). The ages of the firefighters ranged from 32 to 59 years (mean 41.3). The number of years spent firefighting ranged from 5 to 28 years (mean 15 years). The group comprised nine Caucasian males, two Asians (one male, one female) and one African-American male. Seven of the firefighters wore personal protective equipment (PPE) with a self-contained breathing apparatus (SCBA), four did not wear PPE, and one firefighter did not respond to the question. Two firefighters had a history of smoking. All participants were healthy with the exception of the oldest firefighter, a 59-year old Caucasian male who smoked and had a liver condition (hepatitis A).

3.2. Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs)

Of seven PCDDs and 10 PCDFs analyzed in serum, three dioxin isomers, 1,2,3,6,7,8-hexaCDD (HxCDD), 1,2,3,4,6,7,8-heptaCDD (HpCDD), and 1,2,3,4,6,7,8,9-octaCDD (OCDD) were detected in 50, 75, and 100% of the samples, respectively. One PCDF (1,2,3,4,6,7,8-heptaCDF, HpCDF) was detected in 42% of the samples. Congeners 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 1,2,3,4,7,8,9-HpCDF and OCDF were not detected.

ΣPCDD/F concentrations in serum ranged from 183 pg g^{-1} lw to 856 pg g^{-1} lw (mean 447 pg g^{-1} lw, median 310 pg g^{-1} lw) (Tables 1 and SI-2). These concentrations are slightly lower than those reported for the US population (483 pg g^{-1} lw, pooled); however, more congeners were detected in US blood (Schecter et al., 2005). OCDD was the dominant congener in firefighter serum, contributing 55% of the total PCDD/F content, followed by 1,2,3,4,6,7,8-HpCDF (22%) and 1,2,3,4,6,7,8-HpCDD (13%) (Fig. 1a). An interesting finding in this study was the relatively high concentration of HpCDD (mean 87 pg g^{-1} lw, median 77 pg g^{-1} lw) in our samples, which exceeds concentrations of this congener found in the US population (median 28.4 pg g^{-1} lw) (Patterson et al., 2009) and pooled sample 48 pg g^{-1} lw (Schecter et al., 2005) as well as those reported in Taiwanese firefighters (mean 14 pg g^{-1} lw, median 12 pg g^{-1} lw) (Hsu et al., 2011), and high exposure groups of WTC firefighters (mean 45.6 pg g^{-1} lw and 12.2 pg g^{-1} lw) (Horii et al., 2010). HpCDD was previously identified as a possible indicator congener for occupational exposure in firefighter serum (Kelly et al., 2002; Edelman et al., 2003; Chernyak et al., 2012). It is one of the prevalent congeners found on equipment such as face guards after firefighting (along with OCDD, OCDF and 1,2,3,4,6,7,8-HpCDF) (Hsu et al., 2011). Following the WTC fire, 1,2,3,4,6,7,8-HpCDD was the single PCDD congener of those measured that was significantly related to firefighting activity (Edelman et al., 2003). Thus the high concentrations of this congener in the California firefighters may be indicative of occupational exposure.

Combustion processes result in an increase in the relative proportion of PCDFs compared to PCDDs (Hsu et al., 2011). This suggests that currently active firefighters would be expected to exhibit higher concentrations of PCDFs, an effect which we did not observe. However, concentrations of 1,2,3,4,6,7,8-heptaCDF (mean 78 pg g^{-1} lw) were an order of magnitude higher than the concentrations of this congener detected in the US population (pooled sample 3.9 pg g^{-1} lw) (Schecter et al., 2005) and in other firefighters (mean range 6.7–6.9 pg g^{-1} lw) (Hsu et al., 2011; Chernyak et al., 2012).

WHO_{2005}-$TEQ_{PCDD/F}$ concentrations calculated in our samples (mean 5 pg g^{-1} lw, range 1–11 pg g^{-1} lw) were lower than those reported for the US population (17.6 pg g^{-1} lw) (Schecter et al., 2005) and several populations worldwide (Tables 1 and SI-3). The prevalent congener was 1,2,3,6,7,8-HxCDD, accounting for 65% of the total TEQ, followed by 1,2,3,4,6,7,8-HpCDD (17%) and 1,2,3,4,6,7,8-HeptaCDF (16%) (Fig. SI-2). OCDD contributed only 2% of the TEQ because it has a low TEF.

$TEQ_{PCDD/F}$ concentrations in California firefighters were also lower than those reported for other firefighters, including responders to the 2001 WTC fire (mean 41 pg g^{-1} lw) (Horii et al., 2010), and the Taiwanese firefighters and fire investigators (mean 12 pg g^{-1} lw and 15 pg g^{-1} lw, respectively) (Hsu et al., 2011). Higher concentrations in the investigators were attributed to a lack of PPE. In this study, no significant relationship was found between the use of PPE and contaminant concentrations. Much higher $TEQ_{PCDD/F}$ concentrations (mean 122 pg g^{-1} lw) were reported in Russian firefighters who responded to a fire at the Irktuskcable factory in Shelekov, Siberia in 1992, even when measured 11 years after the fire (Chernyak et al., 2004). Concentrations in current Russian firefighters (mean $TEQ_{PCDD/F}$ 12.4 pg g^{-1} lw) were still higher than those in our samples (Chernyak et al., 2012).

3.3. Polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs)

Of six PBDDs and six PBDFs analyzed in serum, one PBDD, 2,3,7,8-tetraBDD (TBDD) was detected in two serum samples, and three PBDFs, 2,3,7,8-tetraBDF (TBDF), 1,2,3,7,8-pentaBDF, and

Table 1
Serum concentrations of halogenated contaminants (mean, median, standard deviation, and range on lipid weight basis) in California firefighters.[a]

Congener or analyte	% Detect	Mean	Median	SD	Range (min–max)
123678-Hexachlorodibenzo-p-dioxin (123678-HxCDD)	50	33	28	25	8–101
1234678-Heptachlorodibenzo-p-dioxin (1234678-HpCDD)	75	87	77	51	26–184
12346789-Octachlorodibenzo-p-dioxin (OCDD)	100	250	194	180	42–674
1234678-Heptachlorodibenzofuran (1234678-HpCDF)	42	78	0	119	nd–342
Sum PCDD/Fs[b]		447	310	256	183–856
$TEQ_{PCDD/F}$		5	5	3	1–11
2378-Tetrabromodibenzo-p-dioxin (2378-TBDD)	17	58	0	134	nd–356
2378-Tetrabromodibenzofuran (2378-TBDF)	8	42	0	145	nd–504
12378-Pentabromodibenzofuran (12378-PeBDF)	17	126	0	303	nd–922
23478-Pentabromodibenzofuran (23478-PeBDF)	17	126	0	312	nd–996
Octabromodibenzofuran (OBDF)	50	2987	2087	1755	1350–5640
Sum PBDD/Fs[b]		3340	2490	2030	1350–7200
$TEQ_{PBDD/F}$		104	1	246	0.2–734
244′-Tribromodiphenyl ether (PBDE-28)	100	2	1	3	0.1–10
22′44′-Tetrabromodiphenyl ether (PBDE-47)	100	52	25	70	5–253
22′44′5-Pentabromodiphenyl ether (PBDE-99)	92	10	6	11	1–41
22′44′6-Pentabromodiphenyl ether (PBDE-100)	100	12	5	16	2–56
22′44′55′-Hexabromodiphenyl ether (PBDE-153)	100	33	20	32	5–98
Decabromodiphenyl ether (PBDE-209)	67	27	24	24	4–88
Sum PBDEs		135	99	112	48–442
22′3-Trichlorobiphenyl (PCB-16)	9	0.2	0	0	nd–2
22′ 34-Tetrachlorobiphenyl (PCB-41)	18	1	0	0	nd–5
22′35-Tetrachlorobiphenyl (PCB-44)	9	1	0	0	nd–6
22′45′-Tetrachlorobiphenyl (PCB-49)	27	1	0	0	nd–2
22′ 5 5′-Tetrachlorobiphenyl (PCB-52)	18	1	0	0	nd–8
2344′-Tetrachlorobiphenyl (PCB-60)	9	0.3	0	0	nd–3
23′44′-Tetrachlorobiphenyl (PCB-66)	9	0.2	0	0	nd–2
23′4′5-Tetrachlorobiphenyl (PCB-70)	9	1	0	0	nd–8
244′ 5-Tetrachlorobiphenyl (PCB-74)	46	2	0	1	nd–7
22′345′-Pentachlorobiphenyl (PCB-87)	27	1	0	0	nd–7
22′356-Pentachlorobiphenyl (PCB-93)	27	2	0	0	nd–13
22′3′45-Pentachlorobiphenyl (PCB-97)	18	1	0	0	nd–4
22′44′5-Pentachlorobiphenyl (PCB-99)	27	1	0	0	nd–7
22′455′-Penthachlorobiphenyl (PCB-101)	27	2	0	0	nd–13
233′44′-Pentachlorobiphenyl (PCB-105)	36	1	0	1	nd–5
233′4′6-Pentachlorobiphenyl (PCB-110)	27	2	0	0	nd–17
23′44′5-Pentachlorobiphenyl (PCB-118)	36	4	0	2	nd–19
22′33′66′-Hexachlorobiphenyl (PCB-136)	9	0.2	0	0	nd–3
22′344′5-Hexachlorobiphenyl (PCB-138)	82	16	14	14	5–34
22′34′55′-Hexachlorobiphenyl (PCB-146)	46	2	0	2	nd–10
22′34′5′6-Hexachlorobiphenyl (PCB-149)	18	2	0	0	nd–16
22′355′6-Hexachlorobiphenyl (PCB-151)	9	0.3	0	0	nd–4
22 ′44′ 5 5′-Hexachlorobiphenyl (PCB-153)	100	27	23	25	11–52
233′44′5-Hexachlorobiphenyl (PCB-156)	73	5	4	4	1–12
22′33 ′44′5-Heptachlorobiphenyl (PCB-170)	91	7	6	7	1–17
22′33′455′-Heptachlorobiphenyl (PCB-172)	18	0.4	0	0	nd–3
22′33 ′4′56-Heptachlorobiphenyl (PCB-177)	64	1	1	1	0.2–3
22′33′55′6-Heptachlorobiphenyl (PCB-178)	46	1	0	1	nd–3
22′344′ 55′-Heptachlorobiphenyl (PCB-180)	100	28	24	26	10–59
22′344′ 5 ′6-Heptachlorobiphenyl (PCB-183)	73	2	1	2	0.2–5
22′34′55 ′6-Heptachlorobiphenyl (PCB-187)	73	6	5	5	1–15
22′33′44′55′-Octachlorobipheynl (PCB-194)	91	5	4	3	0.01–14
22′33′44′56-Octachlorobiphenyl (PCB-195)	18	0.3	0	0	nd–2
22′33′44′56′-Octachlorobiphenyl (PCB-196)	100	3	3	3	1–9
22′33′455′6′-Octachlorobiphenyl (PCB-199)	100	4	3	3	1–10
22′33′55′66′-Octachlorobiphenyl (PCB-202)	82	1	1	1	0.2–4
22′33′44′55′6′-Nonachlorobiphenyl (PCB-206)	64	2	1	2	0.2–9
22′33′44′55′66′-Decachlorobiphenyl (PCB-209)	36	0.4	0	0	nd–2
Sum PCBs		135	126	91	36–317
p,*p*′-Dichlorodiphenyldichloroethylene (*p*,*p*′-DDE)	100	292	249	168	128–662
Hexachlorobenzene (HCB)	100	22	21	11	8–46
Perfluorohexane sulfonate (PFHxS)[c]	100	1	1	1	0.3–2
Perfuorooctane sulfonate (PFOS)	100	12	9	15	3–59
Perfluorodecane sulfonate (PFDS)	17	0.02	0	0.04	nd–0.1
Perfluoroheptanoic acid (PFHpA)	92	0.3	0.3	0.2	0.1–1
Perfluorooctanioic acid (PFOA)	100	7	6	3	2–12
Perfluorononanoic acid (PFNA)	100	2	2	1	1–4
Perfluorodecanoic acid (PFDA)	100	1	1	0.3	0.2–1
Perfluoroundecanoic acid (PFUnDA)	75	0.3	0.2	0.3	0.1–1
Bisphenol-A (BPA)	75	0.4	0.2	1	0.03–1.2

nd = Not detected.
Mean lipid of sample = 0.4%.
[a] Values are expressed as ng g^{-1} lipid weight unless otherwise indicated.
[b] Units for dioxins and furans are pg g^{-1} lipid weight.
[c] Units for PFCs and BPA are expressed as ng ml^{-1} wet weight.

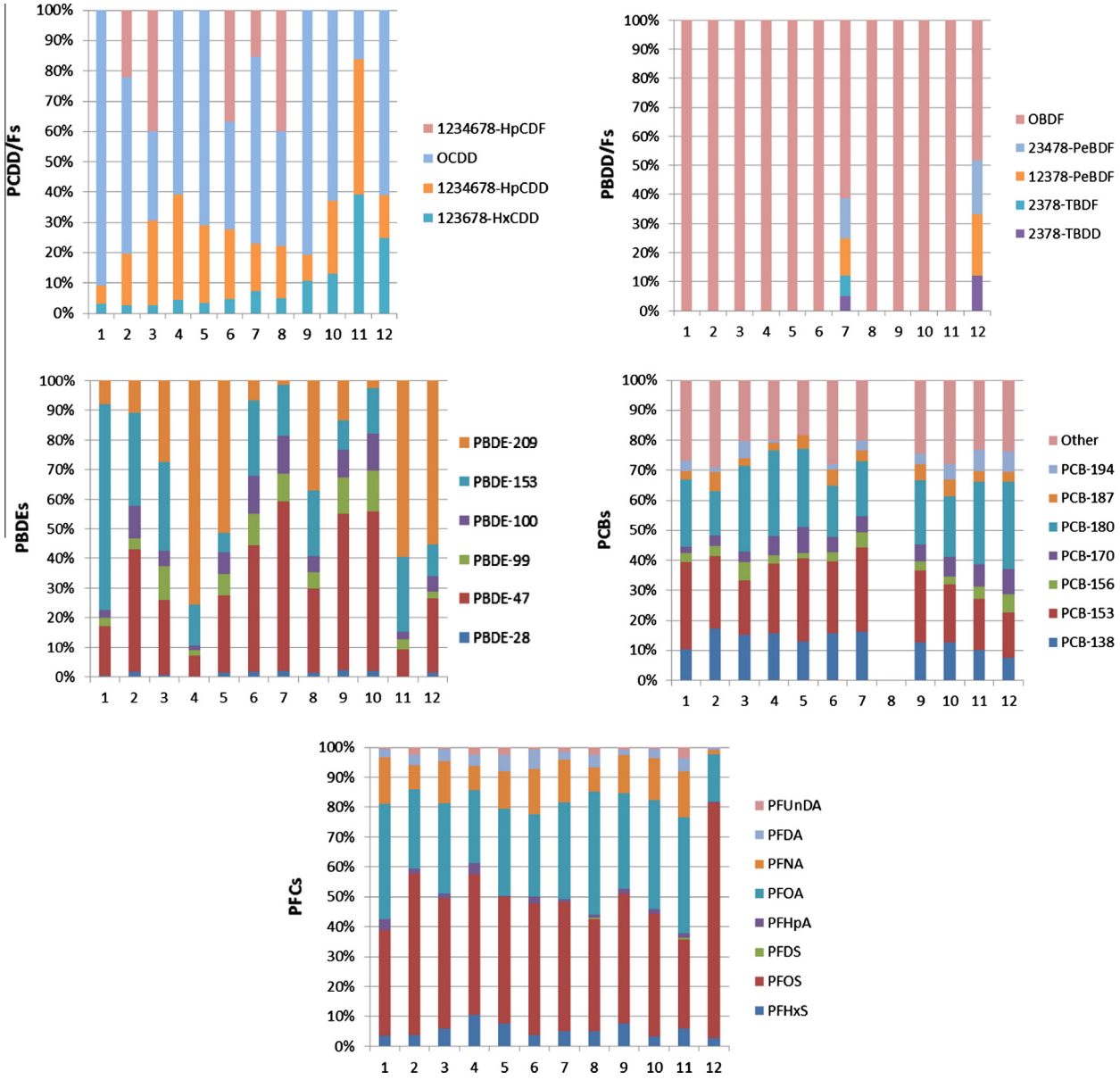

Fig. 1. Congener profiles in serum of California firefighters for PCDD/Fs, PBDD/Fs, PBDEs, PCBs, and PFCs.

2,3,4,7,8-pentaBDF, were detected in one or two samples. 1,2,3,4,6,7,8,9-octaBDF (OBDF) was detected in 50% of the samples.

ΣPBDD/F concentrations in serum of the California firefighters were relatively high, ranging from 1350–7200 pg g^{-1} lw (mean 3340 pg g^{-1} lw, median 2490 pg g^{-1} lw) (Tables 1 and SI-4). In contrast to the predominance of PCDDs in serum, PBDFs contributed the majority of the total PBDD/F content, with OBDF accounting for 92%. Interestingly, the four other detected congeners were present only in two individuals: the oldest firefighter, a 59-year old Caucasian male with the longest record of firefighting (28 years) and who smoked and had hepatitis A, and a 40-year old Caucasian male who had been firefighting for 15 years (Fig. SI-4b). This individual reported that he was heavily exposed to dust and smoke, did not wear PPE with a self-contained breathing apparatus (SCBA), and was responsible for breaking into the roof and clean-up (overhaul) of fires.

Concentrations of the congener 2,3,7,8-TBDD (mean 58 pg g^{-1} lw) in these samples were similar to those reported in German plant workers conducting extrusion and blending of polybutyleneterephthalate with deca-BDE (median 40 pg g^{-1} lw) (Zober et al., 1992). However, 2,3,7,8-TBDF was the only PBDF reported in the extruder workers (median 8 pg g^{-1} lw) and concentrations of this congener in the two California firefighters were much higher (mean 42 pg g^{-1} lw). ΣPBDD/F concentrations in our samples were orders of magnitude higher than the population concentrations reported for Sweden and Japan (Choi et al., 2003; Jogsten et al., 2010). The high concentrations of PBDFs in the two individual firefighters confirm previous observations that individual exposure during firefighting may be quite variable.

In the absence of WHO TEFs for PBDD/Fs, values for chlorinated analogues were used to calculate TEQs. Some of the values are only approximations and must be considered as indicative. WHO_{2005} $TEQ_{PBDD/F}$ concentrations in firefighter serum (mean 104 pg g^{-1} lw) were 21 times higher than the $TEQ_{PCDD/F}$ (5 pg g^{-1} lw) (Table 1). While preliminary, this finding suggests that occupational exposure to PBDD/Fs formed during fires may pose a significant health risk to firefighters. The brominated congener 2,3,7,8-TBDD contributed the majority (55%) of the $TEQ_{PBDD/F}$ content, followed by

2,3,4,7,8-pentaBDF (36%) (Fig. SI-2). $TEQ_{PBDD/F}$ concentrations in the California firefighters were similar to those reported for German extruder operators (median 116 pg g^{-1} lw) (Table SI-5), and were several orders of magnitude higher than those reported in Swedish adipose tissue (Jogsten et al., 2010) and human milk samples (Kotz et al., 2005). Although 2,3,7,8-TBDF, 1,2,3,7,8-pentaBDF, and 2,3,4,7,8-pentaBDF were present in Swedish tissue, OBDF and 2,3,7,8-TBDD were not detected, implying that the distinctive PBDD/F congener patterns in the firefighters resulted from occupational exposure.

3.4. Other persistent organic pollutants (POPs)

Other POPs detected in serum of the firefighters were, in descending order of concentrations: *p,p′*-DDE > PBDEs = PCBs > HCB > PFCs (Table 1). TBBPA was not detected in any samples. BPA was a minor contaminant in serum (Table SI-9 and discussion in Supplementary Materials). The Spearman's rank correlation test revealed intercorrelations between ΣPCDD/Fs and PBDE-153 ($r = 0.8$, $p = 0.03$), between PCB (hepta-CB) congeners and *p,p′*-DDE ($r = 0.5$, $p = 0.04$) between ΣPCBs and PFOA ($r = 0.6$, $p = 0.04$), and between several PBDE and PFC congeners (e.g. PFHxS and PBDE-209; $r = 0.9$, $p \leqslant 0.0001$) possibly indicating similar sources or exposure pathways for the compounds.

3.4.1. Polybrominated diphenyl ethers (PBDEs)

Of nine congeners analyzed, PBDE congeners −99 and −209 were detected in 92% and 67% of the samples, respectively, and congeners −28, −47, −100, and −153 were detected in 100% of the samples. PBDE-66, -85, and -154 were not detected.

The sum of tri- through deca-BDE congener concentrations in serum ranged from 48 ng g^{-1} lw to 442 ng g^{-1} lw (mean 135 ng g^{-1} lw, median 99 ng g^{-1} lw) (Table 1). These concentrations were two to threefold greater than those reported for the general US population (mean range 38.6–61.8 ng g^{-1} lw) (Schecter et al., 2005; Anderson et al., 2008; Zota et al., 2008; Johnson et al., 2010) and residents of California (62 ng g^{-1} lw) (Zota et al., 2008) (Table SI-6). Concentrations in the firefighters were much higher than those reported in human blood from Asian and European countries.

ΣPBDE concentrations in the firefighters were lower than those found in carpet layers (median 178 ng g^{-1} lw) and foam recyclers (median 160 ng g^{-1} lw) from California and Maryland (Stapleton et al., 2008), and much lower than the concentrations reported in e-waste recyclers from Guiyu, south China (median 600 ng g^{-1} lw) (Bi et al., 2007).

Low to medium-brominated PBDEs (tri- to hexa-) are generally the major congeners in environmentally (non-occupationally) exposed humans (She et al., 2002; Hites, 2004), while highly brominated PBDEs are often elevated in occupationally exposed groups such as electronics-dismantling workers (Thomsen et al., 2001; Thuresson et al., 2005). The importance of inhalation has been emphasized in occupational exposure (Thuresson et al., 2005). Following restriction of penta-BDE mixtures in many countries, PBDE-153, a constituent of commercial octa-BDE, has emerged as a major PBDE congener in non-occupationally exposed populations (Bi et al., 2006; Thomas et al., 2006; Jogsten et al., 2010). However, PBDE-153 was also reportedly a major contaminant, along with PBDE-183, in electronic dismantlers from Sweden (Sjödin et al., 1999). PBDE-209, the major constituent of deca-BDE, is rarely detected in non-occupationally exposed humans, but has been specifically related to occupational exposure in several studies (Thomsen et al., 2001; Thuresson et al., 2005; Bi et al., 2007; Stapleton et al., 2008).

The PBDE congener profiles in the California firefighters differed from the pattern found in the general population (Fig. 1c). PBDE-47 and -209 were prevalent congeners, accounting for 32% and 29% of the total PBDE concentration, respectively, followed by PBDE-153 (23%). However, an elevated concentration of PBDE-47 (253 ng g^{-1} lw) found in one individual qualified as an outlier, since it was >2 times the standard deviation of the mean concentration. When this outlier was excluded, PBDE-209 was the predominant congener in serum, contributing 32% to the total concentration. PBDE congeners −99 and −100, constituents of penta-BDE, were detected at low concentrations in firefighter serum, but they are prevalent congeners, along with PBDE-47, in non-occupationally exposed subjects (Johnson-Restrepo et al., 2005; Thomas et al., 2006). PBDE-209 concentrations in the firefighters (mean 27 ng g^{-1} lw) were lower than those previously reported in rubber workers exposed to commercial deca-BDE in Sweden (mean 77 ng g^{-1} lw) (Thuresson et al., 2005) and the very high concentrations found in e-waste recyclers in Guiyu (mean 340 ng g^{-1} lw) and residents of Haojiang, China (mean 130 ng g^{-1} lw) (Bi et al., 2007).

The elevated concentrations of ΣPBDEs and unique congener profiles in the 12 firefighters are suggestive of occupational exposure to all three PBDE formulations (Figs. SI-3c and SI-4c). Since PBDE-209 has a short half-life in serum (approximately 15 d) (Thuresson et al., 2006), their relatively high PBDE-209 concentrations imply that these firefighters are continuously exposed to deca-BDE. The highest PBDE-209 concentration (88 ng g^{-1} lw) was detected in a Caucasian male firefighter aged 34 who had been firefighting for five years without wearing PPE. PBDE-209 contributed 75% of the total PBDE content in this individual, and >50% of the total in three other firefighters (Fig. 1c). Inhalation of large amounts of smoke and dust while firefighting was reported by all subjects in this study. As PBDE-209 is strongly particulate-associated, the relatively high PBDE-209 concentrations in the firefighters may result from inhalation of deca-BDE-containing particulate in smoke and dust released from burning televisions, computers, and carpets.

3.4.2. PCBs and organochlorine pesticides

Of 109 PCBs analyzed (di-to deca congeners) in serum, 21 congeners or co-eluted pairs were detected in at least 50% of the samples (PCB-138/164/163/158, 153/132/168, 156, 170/190, 177, 180, 183, 187/182, 194, 196/203, 199, 202, and 206), accounting for 50–100% of the total PCB content. Sixty-eight congeners or co-eluted pairs were detected in at least one sample.

ΣPCB concentrations in firefighter serum (mean 135 ng g^{-1} lw, median 126 ng g^{-1} lw, range 36–317 ng g^{-1} lw) were lower than the median concentrations reported for the general US population (154 ng g^{-1} lw) (Patterson et al., 2009), Massachusetts residents (212 ng g^{-1} lw) (Meeker et al., 2007) and the UK population (170 ng g^{-1} lw) (Thomas et al., 2006) (Tables 1 and SI-7). Concentrations in the firefighters were similar to those reported in adipose tissue samples from New York (mean 144 ng g^{-1} lw) (Johnson-Restrepo et al., 2005) but lower than the concentrations reported in human blood sampled in the 1990s (Kärrman et al., 2006; Sawada et al., 2010), suggesting that PCBs are declining in Americans (Sjödin et al., 2004). Lower PCB concentrations were found in residents of an e-waste recycling region of China, reflecting the low PCB usage in China (Bi et al., 2007). Inuit populations have the highest PCB concentrations owing to their consumption of contaminated marine mammals (Dallaire et al., 2009).

PCB profiles in firefighters are not usually considered to be indicative of exposure routes since the profiles formed during combustion are similar to those from environmental and technical mixtures (Chernyak et al., 2012). PCB congener profiles in the 12 California firefighters were fairly similar (Fig. 1d). PCB-180 was the predominant congener, accounting for 23.6% of the total concentration, followed by PCB-153 (22.7%), PCB-138 (13%), and PCB-170/190 (5.8%). PCB-187, -156, and -194 each contributed 3–4% to the total. A similar profile dominated by PCB-180 was

recently reported in plasma samples of Hong Kong residents (Qin et al., 2011). This differs from the pattern generally found in humans, which is dominated by PCB-153 and -138 (Johnson-Restrepo et al., 2005; Bi et al., 2007), and suggests that PCB profiles may be shifting in human tissue.

Although DDT was banned in the US in 1973, the persistent metabolite *p–p′*-DDE was detected in every firefighter sample at concentrations ranging from 128–662 ng g^{-1} lw (mean 292 ng g^{-1} lw, median 249 ng g^{-1} lw) (Table 1 and Fig. SI-3e). These concentrations were slightly higher than those reported for the US population and Massachusetts residents sampled between 2000 and 2004 (median 203–204 ng g^{-1} lw, respectively) (Meeker et al., 2007; Patterson et al., 2009) (Table SI-7). Higher concentrations (337 ng g^{-1} lw) were reported for the US population sampled in 2001–2002 (Turyk et al., 2007), reflecting a gradual decline of *p–p′*-DDE in the US. Much higher *p–p′*-DDE concentrations have been reported in populations where DDT is still in use (Bi et al., 2007; Zamir et al., 2009; Qin et al., 2011). Elevated *p–p′*-DDE concentrations in the Inuit are attributed to dietary exposure (Dallaire et al., 2009).

HCB, a seed crop fungicide that was banned in the US in 1984, was detected in 100% of the firefighter samples at concentrations ranging from 8 ng g^{-1} lw to 46 ng g^{-1} lw (mean 22 ng g^{-1} lw, median 21 ng g^{-1} lw) (Table 1 and Fig. SI-3f). HCB concentrations in the firefighters were higher than serum concentrations reported for the US and UK populations (median range 11–14.9 ng g^{-1} lw) (Thomas et al., 2006; Meeker et al., 2007; Patterson et al., 2009), but much lower than concentrations reported in human blood sampled in the 1990s (Kärrman et al., 2006; Sawada et al., 2010) (Table SI-7), suggesting that HCB concentrations are declining. Higher HCB concentrations were reported in blood of Chinese e-waste recyclers (Bi et al., 2007) and the Inuit (Dallaire et al., 2009).

3.4.3. Perfluorinated compounds (PFCs)

PFCs are used in consumer products such as soil- and stain-resistant coatings on upholstery, carpets, leather, floor waxes, polishes, and in fire-fighting foams, and are potentially released during fire events, resulting in exposure of firefighters to these compounds. Of 11 PFCs analyzed in serum of the California firefighters, eight compounds were detected. Perfluorooctanesulfonate (PFOS), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorohexane sulfonate (PFHxS), and perfluorodecanoic acid (PFDA) were detected in 100% of the samples. Perfluoroheptanoic acid (PFHpA), perfluoroundecanoic acid (PFUnDA), and perfluorodecane sulfonate (PFDS) were detected in 92, 75, and 17% of the samples, respectively. Perfluorobutane sulfonate (PFBS), perfluorooctane sulfonamide (PFOSA) and perfluorododecanoic acid (PFDoDA) were not detected in any sample.

PFOS was the prevalent PFC in firefighter serum, ranging from 3 ng ml^{-1} ww to 59 ng ml^{-1} ww (mean 12 ng ml^{-1} ww, median 9 ng ml^{-1} ww), followed by PFOA, ranging from 2 ng ml^{-1} ww to 12 ng ml^{-1} ww (mean 7 ng ml^{-1} ww, median 6 ng ml^{-1} ww), and PFNA, ranging from 1 ng ml^{-1} ww to 4 ng ml^{-1} ww (mean 2 ng ml^{-1} ww, median 2 ng ml^{-1} ww). Minor PFCs in serum were PFHxS (mean 1 ng ml^{-1} ww, median 1 ng ml^{-1} ww), and PFDA (mean 1 ng ml^{-1} ww, median 1 ng ml^{-1} ww) (Table 1 and Fig. 1e). Compared to concentrations in the US population sampled in 2003–2004 (Calafat et al., 2007), PFOS and PFHxS concentrations were approximately twofold lower and PFOA and PFNA concentrations were twofold higher in the firefighters (Table SI-8).

Median concentrations of PFOS, PFOA, and PFHxS in our samples were two to four times lower than mean concentrations reported in plasma of WTC responders (Tao et al., 2008). Following the WTC collapse, PFNA concentrations were elevated in the responders exposed to high levels of smoke (Tao et al., 2008). PFNA concentrations in the California firefighters were even higher than those in the WTC responders (mean 2 ng ml^{-1} versus 1.0 ng ml^{-1} ww), thus, it is plausible that they were exposed to PFNA in smoke during firefighting. PFOA and PFHxS concentrations were also higher in smoke-exposure versus dust exposure groups of WTC responders, suggesting that these compounds are concentrated in smoke during fires (Tao et al., 2008). Although PFOA concentrations in the California firefighters were lower than those in the WTC responders, they exceeded US population concentrations, implying that the firefighters were occupationally exposed to PFOA as well as PFNA.

3.4.4. Factors influencing contaminant concentrations

Due to the small sample size and our inability to adjust for potential confounding variables, it was not possible to draw reliable conclusions about the influence of age, gender, firefighting roles, use of PPE, or other factors on contaminant concentrations in the firefighters. However, the Mann–Whitney *U* test showed that the two Asian firefighters, both of whom were relatively young, had significantly higher serum concentrations of OCDD, PBDE-153 and HCB (all $\chi^2 = 4.62$, $p = 0.03$) than the other firefighters (Fig. SI-1). Interestingly, the Asian male firefighter (age 33) had the highest concentration of ΣPCBs (317 ng g^{-1} lw), while the Asian female firefighter (age 32) had the highest concentration of OCDD (674 pg g^{-1} lw) and a relatively high level of OBDF (4982 pg g^{-1} lw) compared with the other firefighters. The female had been firefighting for 7 years and did not use PPE, whereas the Asian male had been firefighting for 11 years and did use PPE, and additionally, their firefighting roles differed. The explanation for higher concentrations of these compounds in the Asians is unclear, but they may, in part, reflect cultural differences in environmental exposures, such as seafood consumption.

4. Conclusions

This is the first study to report the exposure of firefighters to both PCDD/Fs and PBDD/Fs which can be released in large amounts during residential and commercial fires. Although the data are preliminary and limited by the small sample size, elevated concentrations of specific congeners indicative of firefighting were identified in serum. Tentative TEQs calculated for PBDD/Fs suggested that these compounds may contribute substantially to dioxin-like toxicity in individual firefighters. The elevated concentrations of PBDEs in the California firefighters relative to US population concentrations and the distinctive PBDE and PFC congener patterns in serum are suggestive of significant occupational exposure to these compounds during firefighting.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2012.12.070.

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