



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



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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 WHO₂₀₀₅-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.

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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),

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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, PBDEs 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, anti-estrogen 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 WHO₂₀₀₅-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

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