WHEN FLAME RETARDANTS BURN: EXPOSURE TO COMBUSTION BY-PRODUCTS AND CANCER RISK AMONG FIRE FIGHTERS

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Introduction

Firefighters inhale, ingest, and absorb hundreds of toxic, carcinogenic chemicals in smoke and soot during every phase of firefighting – suppression, knockdown/ventilation, and overhaul (clean-up). Fires today are more toxic than in the past because of the high usage of halogenated chemicals including brominated flame retardants (BFRs) in furniture, electronics, plastics, and other consumer products[1]. In the presence of high concentrations of bromine-containing materials, a major concern during fire events is the potential formation of large amounts of combustion by-products such as brominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs)[1-3]. PBDD/Fs are formed during fires under uncontrolled combustion conditions in the presence of chemical precursors such as the polybrominated diphenyl ethers (PBDEs) [2-4] PBDD/Fs are major contaminants both indoors and in the environment[5], and contribute substantially to total dioxin-like toxicity in house dust[6], in food[7] and in human tissues[8,9].

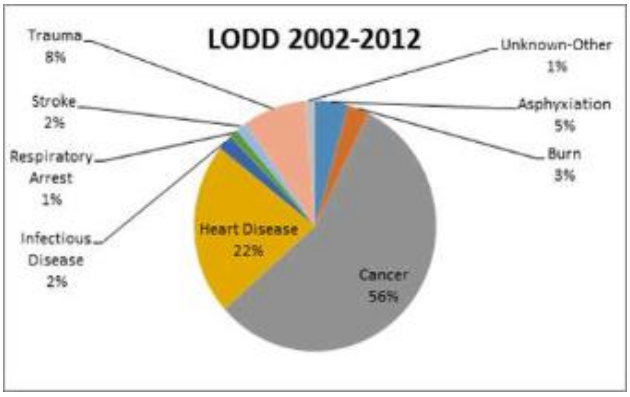

Figure 1. Cancer is the leading cause of line-of-duty deaths (LODDs) in the fire service today[10].

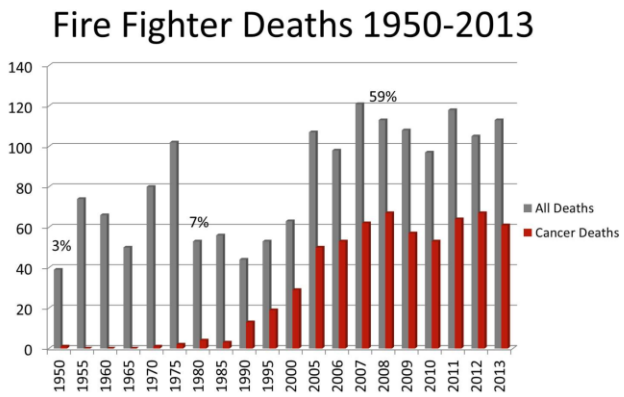

Figure 2. Since 1990, cancer-related mortalities among fire fighters have increased exponentially, accounting for 50-60% of all LODDs since 2005.

Fire fighters have elevated rates of multiple cancers thought to be related to their occupational exposure to carcinogenic chemicals. In 2007, the International Agency for Research on Cancer classified firefighting as possibly carcinogenic to humans (Group 2B); relative risks were consistently increased for testicular cancer, prostate cancer, and non-Hodgkin's lymphoma[11,12]. A meta-analysis of 32 studies of firefighters reported increased risks for these tumors as well as multiple myeloma[13]. A large-scale epidemiological study conducted by NIOSH, the National Cancer Institute, and the University of California-Davis reported higher risks of digestive, oral, respiratory, and urinary system cancers among 29,993 firefighters in Chicago, Philadelphia, and San Francisco than among the general population[14]. A recent study[15] of 16,422 male Nordic fire fighters from five countries reported increased risk among fire fighters for prostate cancer and skin melanoma in fire fighters ages 40-49, and increased risk for multiple myeloma, adenocarcinoma of the lung, and mesothelioma in older fire fighters (70 years and above). Overall, the

data show that fire fighters are at increased risk for multiple cancers and their cancer risk increases significantly with the duration of firefighting.

Most investigations of fire fighter exposure have focused on a limited number of compounds (e.g., polychlorinated biphenyls, PCBs, PCDD/Fs) following acute fire events[16-20]. A recent pilot study of fire fighters from northern California represents the most extensive exposure assessment among fire fighters to date[22]. The California study was the first to analyze PBDD/Fs, along with PCDD/Fs, PBDEs, perfluorinated chemicals (PFCs), *p-p'*-DDE, hexachlorobenzene (HCB), tetrabromobisphenol-A (TBBPA) and bisphenol-A (BPA) in serum of fire fighters after a fire event.

Materials and methods

Samples. Venous blood samples (100 ml) were collected from 12 veteran fire fighters within 24 h of responding to a fire. Participants (1) had not worked in industries with known chemical emissions; (2) were fire fighters for at least 5 years; and (3) had responded to fire scenes at least 20 times in the past 5 years. Blood was spun down to approximately 40 mL serum, and kept frozen at -20° C until analysis.

Chemical analysis. Congener-specific concentrations of PBDD/Fs, PCDD/Fs, PBDEs, and PCBs 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, U.S.A.) (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 (Wellingtion Laboratories, Ontario, Canada) and d_{16}-BPA (Cambridge Isotope Laboratories, Andover, MA, U.S.A.) were used as internal standards for isotopic dilution method.

Results and discussion

PBDEs. PBDE levels in fire fighter serum were two to three times greater than average levels in the US population[23,24] and California residents[24]. BDE-209 was the predominant congener, contributing, on average, 32% to the total PBDE content, followed by BDE-47 and -153. Given the short half-life of BDE-209 in serum[25], this pattern implies ongoing exposure to DecaBDE during firefighting. Similarly, DecaBDE dominates the PBDE profiles in blood of e-waste recyclers engaged in open burning of plastic TVs and computers[26].

PBDD/Fs. PBDD/F concentrations in fire fighter serum were similar to occupational levels in foam workers and 70-100 times higher than those in the general population (Table 1). Four detected PBDD/F congeners were present in two individuals: a 59-year old Caucasian male with the longest record of firefighting (28 years), who smoked and had hepatitis A, and a 40-year old Caucasian male who had been firefighting for 15 years without wearing personal protective equipment (PPE).
PBDD/F dioxin-like toxicity (mean 103 pg/g lw WHO-TEQ) in fire fighter serum was 21 times higher than that of PCDD/Fs (5 pg/g lw WHO-TEQ), and 1000 times higher than average population levels (Table 1), suggesting that exposure to PBDD/Fs may pose a significant health risk to individual fire fighters.

PCDD/Fs. PCDD/F concentrations in fire fighter serum were relatively low (mean 5 pg/g lw WHO-TEQ); however, concentrations of 1,2,3,4,6,7,8-HpCDD exceeded levels of this congener reported in World Trade Center (WTC) responders[17]. HpCDD has been identified as a possible indicator congener in fire fighters[16].

Results and discussion, continued

PFCs. PFOS was the prevalent PFC in firefighter serum (mean 12 ng/ml wet weight, ww), followed by PFOA (7 ng/ml ww), and PFNA (2 ng/ml ww). PFOA and PFNA concentrations were elevated relative to average population levels[27]. PFNA levels were also higher than those reported in World Trade Center fire fighters[20].

Other POPs. p-p'-DDE and HCB in firefighter serum were similar to average US population levels[28] and PCB congener profiles were not indicative of occupational exposure. TBBPA was not detected; BPA was detected at trace levels in firefighter serum.

Table 1. Comparison of PBDD/F concentrations (pg/g lw) in fire fighters, foam workers, and general population

Population	Location	Year	Tissue	2378-TBDD	2378-TBDF	12378-PeBDF	23478-PeBDF	ΣPBDD/F	TEQ	Ref
Firefighters	California	2009	serum	58 (nd-356)	42 (nd-504)	126 (nd-922)	126 (nd-996)	352	103[c]	22
Extruder operators	Germany	1990-91	blood	40 (nd-478)	8 (nd-112)				41[c]	29[a]
General pop.	Sweden	2007	adipose	nd	0.7 (0.3-2.2)	0.1 (nd-0.9)	0.1 (nd-0.5)	1 / 2.3	0.5/0.6[d]	8[b]
General pop.	Japan	1970	adipose	1.7 (nd-4.2)	3.3 (1.6-4.3)		0.3 (0.3-0.6)	5.1	2.1[c]	6
General pop.	Japan	2000	adipose	0.51 (0.1-2)	2.8 (1.7-4.2)		1 (nd-1.9)	3.4	1.1[c]	6
General pop.	Various		milk	(0.1-0.3)	0.7 (nd-2.7)		0.2 (nd-1.1)		0.3/1.1[e]	9

[a] Data from foam workers in a plant that does extrusion and blending of polybutyleneterephthalate with DecaBDE
[b] Lower bound (excluding <= values)/ Upper bound (including <= values)
[c] TEQ calculated with PCDD/F WHO_{2005} TEFs (Van den Berg et al 2006); [d] TEQ calculated with PBDD/F REPs (Samara et al 2009);
[e] TEQ calculated with PCDD/F WHO_{1998} TEFs (Van den Berg 1998); see discussion of TEQ calculations in Shaw et al. (2013).
nd= not detected

Conclusions. Overall, the data indicate that occupational exposure to flame retardants and combustion by-products places fire fighters at increased risk for cancer, stroke, and other serious health effects. The California study showed that fire fighters accumulate high serum concentrations of PBDEs, PBDD/Fs, and PFCs while firefighting, and that PBDD/Fs may contribute substantially to dioxin-like toxicity in individual firefighters. The predominance of DecaBDE (BDE-209) in fire fighter blood suggests that they are continuously exposed to DecaBDE released from burning plastics. Elevated PFOA and PFNA concentrations in fire fighter blood implies that firefighting involves substantial exposure to long-chain PFCs currently used as replacements for banned PFCs.

Based on preliminary exposure data and the elevated rates of multiple cancers among fire fighters today, a large-scale, longitudinal study is planned to examine chemical exposure and biomarkers of health effects including pre-cancer and cancer markers in fire fighters at municipalities across the US.

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