Persistent Organic Pollutants Including Polychlorinated and Polybrominated Dibenzo-p-dioxins and Dibenzofurans in Firefighters from Northern California

Susan D. Shaw[1,3], Michelle L. Berger[1], Jennifer H. Harris[1], Se Hun Yun[2],Qian Wu[2,3], Chunyang Liao[2], Arlene Blum[4], Anthony Stefani[5], and Kurunthachalam Kannan[2,3]

[1] Marine Environmental Research Institute, Center for Marine Studies, P.O. Box 1652, Blue Hill, ME 04614, USA; [2] Wadsworth Center, New York State Department of Health, Albany, NY 12201, USA; [3] 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; [4] Green Science Policy Institute, University of California, Berkeley, CA, USA; [5]San Francisco Firefighters Cancer Prevention Foundation, 1139 Mission St., San Francisco CA 94103, USA

Introduction

Firefighters are exposed to a wide range of toxic chemicals both during and while cleaning up after fires. Of major concern are the carcinogenic combustion by-products formed during fires such as chlorinated and brominated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs and PBDD/Fs)[1-3]. Elevated rates of cancer have been reported in firefighters including four types that are potentially related to exposure to dioxins and furans – multiple myeloma, non-Hodgkin's lymphoma, prostate, and testicular cancer[4-7]. Whereas previous investigations of firefighters have focused on exposure to PCDD/Fs, PBDD/Fs are major contaminants both indoors and in the environment[2], and large amounts can be formed during fires in the presence of polybrominated dipheny ethers (PBDEs)[1,2,8,9]. This study analyzed PBDD/Fs and PCDD/Fs, along with PBDEs, perfluorinated chemicals (PFCs), polychlorinated biphenyls (PCBs), *p,p'*-DDE, hexachlorobenzene (HCB), tetrabromobisphenol A (TBBPA), and bisphenol-A (BPA) in serum of twelve firefighters sampled after a fire event in San Francisco, California.

Materials and Methods

Study subjects and sampling. Twelve firefighters selected for the study (1) had not worked in industries with known chemical emissions; (2) were firefighters for at least 5 years; and (3) had responded to fire scenes at least 20 times in the past 5 years. Personal characteristics, health and work history data were collected by questionnaire. Blood samples (100 mL) were collected within 24 h of responding to a fire, and spun down to ~40mL serum. Samples were frozen at -20^{o}C and shipped overnight for analysis.

Chemical analysis. Concentrations of PCDD/Fs, PBDD/Fs, PBDEs, PCBs, *p,p'*-DDE, and HCB were determined in serum by high resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS) using methods described elsewhere, with modifications[10-12]. Concentrations of PFCs, TBBPA, and BPA were determined by high-performance liquid chromatography tandem mass spectrometry (HPLC-MS/MS) using methods described elsewhere, with modifications[13].

Statistical analysis. Data were analyzed using SPSS (version 15.0, SPSS, Inc., Chicago, IL). 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. Dioxin toxic equivalents (TEQs) were calculated for PCDD/Fs using WHO_{2005} toxic equivalency factors (TEFs)[14]. TEQs were calculated for PBDD/Fs using WHO_{2005} TEFs for chlorinated analogues.

Table 1. Serum concentrations of halogenated contaminants (mean and range) in California firefighters

Compound	% Detect	Mean	Range
PCDD/Fs (pg/g lw)			
1,2,3,6,7,8-HexaCDD (HxCDD)	50%	33	8-101
1,2,3,4,6,7,8-HeptaCDD (HpCDD)	75%	87	26-184
1,2,3,4,6,7,8,9-OctaCDD (OCDD)	100%	250	42-674
1,2,3,4,6,7,8-HeptaCDF (HpCDF)	42%	78	nd-342
Sum PCDD/F		447	183-856
WHO_{2005} TEQs of PCDD/Fs		5	1-11
PBDD/Fs (pg/g lw)			
2,3,7,8-TetraBDD (TBDD)	17%	58	nd-356
2,3,7,8-TetraBDF (TBDF)	8%	42	nd-504
1,2,3,7,8-PentaBDF	17%	125	nd-922
2,3,4,7,8-PentaBDF	17%	126	nd-996
1,2,3,4,6,7,8,9-OctaBDF (OBDF)	50%	2987	1350-5640
Sum PBDD/F		3340	1350-7200
WHO_{2005} TEQs of PBDD/Fs		104	0.2-734
PBDEs (ng/g lw)			
PBDE-28	100%	12	2-56
PBDE-47	100%	52	5-253
PBDE-99	92%	10	1-41
PBDE-100	100%	12	2-56
PBDE-153	100%	33	5-98
PBDE-209	67%	27	4-88
Sum PBDE (tri-deca)		135	48-442
PFCs (ng/ ml ww)			
Perfluorohexane sulfonate (PFHxS)	100%	1	0.3-2
Perfluorooctanesulfonate(PFOS)	100%	12	3-59
Perfluorodecane sulfonate (PFDS)	17%	0.02	nd-0.1
Perfluoroheptanoic acid (PFHpA)	92%	0.3	0.1-1
Perfluorooctanoic acid (PFOA)	100%	7	2-12
Perfluorononanoic acid (PFNA)	100%	2	1-4
Perfluorodecanoic acid (PFDA)	100%	1	0.2-1
Perfluoroundecanoic acid (PFUnDA)	75%	0.3	0.1-1

Table 2. PBDD/F concentrations (pg/g lw) in human tissues

Population	Location	Year	Tissue	2378-TBDD	2378-TBDF	12378-PeBDF	23478-PeBDF	OBDF	ΣPBDD/F	Ref
Firefighters	California	2009	serum	58 (nd-356)	42 (nd-504)	126 (nd-922)	126 (nd-996)	2987(1350-5640)	3340	
Extruder operators	Germany	1990-91	blood	40 (nd-478)	8 (nd-112)					25[a]
Maint. mechanics	Germany	1990-91	blood	17 (17-22)	16 (nd-26)					25[a]
Production	Germany	1990-91	blood	28 (7-48)	7 (7-7)					25[a]
R+D personnel	Germany	1990-91	blood	nd (nd-5)	2 (nd-11)					25[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	26[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	27
General pop.	Japan	2000	adipose	0.51 (0.1-2)	2.8 (1.7-4.2)		1 (nd-1.9)		3.4	27
General pop.	Various		milk	(0.1-0.3)	0.7 (nd-2.7)		0.2 (nd-1.1)			28

[a] These data are from workers in a plant that does extrusion and blending of polybutyleneterephthalate with decaBDE
[b] Lower bound (excluding <- values)/ Upper bound (including <- values)
nd= not detected

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For more information, please contact Dr. Susan Shaw at sshaw@meriresearch.org

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Results and Discussion

Study Population

The group comprised nine Caucasian males, two Asians (one male, one female) and one African-American male. Ages ranged from 32 to 59 years (mean age 41.3). The number of years spent firefighting ranged from 5 to 28 years (mean 15 years). 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 hepatitis A.

PCDD/Fs

- PCDD/F concentrations in serum were relatively low (mean 5 pg/g lw WHO-TEQ) (Table 1) compared with average US population levels (17.6 pg/g lw)[15], and levels reported in studies of other firefighters[16,17].
- Concentrations of 1,2,3,4,6,7,8-HpCDD exceeded levels of this congener reported in other firefighters, including responders to the 2001 World Trade Center (WTC) fire[17] (Fig. 1). HpCDD has been identified as a possible indicator congener in firefighters[18].

PBDD/Fs

- ΣPBDD/F concentrations in firefighter serum (mean 3340 pg/g lw) were relatively high on a global scale (Table 2).
- OBDF accounted for 92% of the PBDD/F content (Fig. 1). Four other detected congeners were present only in two individuals: the 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 PPE.
- Dioxin-like toxicity of PBDD/Fs in serum (mean 104 pg/g lw WHO-TEQ) was 21 times higher than that of PCDD/Fs (Table 1), suggesting that exposure to PBDD/Fs may pose a significant health risk to individual firefighters.

PBDEs

- ΣPBDE (tri- through deca-BDE) concentrations in firefighter serum (mean 135 ng/g lw) (Table 1) were two to three times greater than average levels in the US population[15, 19] and California residents[19] and the distinctive PBDE congener profiles in the firefighters suggested occupational exposure.
- BDE-209 was the predominant congener, contributing 32% to the total PBDE content, followed by BDE-47 and -153. Given the short half-life of BDE-209 in serum[20] this pattern implies ongoing exposure to deca-BDE during firefighting, similar to the profiles in blood of e-waste recyclers engaged in open burning of plastic TVs and computers[21].

PFCs

- PFOS was the prevalent PFC in firefighter serum (mean 12 ng/ml wet weight, ww), followed by PFOA (mean 7 ng/ml ww), and PFNA (mean 2 ng/ml ww) (Table 1, Fig. 1).
- PFOA and PFNA concentrations were two-fold higher in the firefighters than average US population levels[22].
- PFNA and PFOA were also elevated in the high smoke-exposure group of the WTC fire responders[23], implying that the California firefighters were exposed to these PFCs via smoke inhalation during firefighting.

Other POPs

- Concentrations of ΣPCBs and organochlorine pesticides (*p-p'*-DDE and HCB) in firefighter serum were similar to average US population levels[24] and PCB congener profiles were not indicative of occupational exposure.
- TBBPA was not detected; BPA was detected at trace levels in firefighter serum.

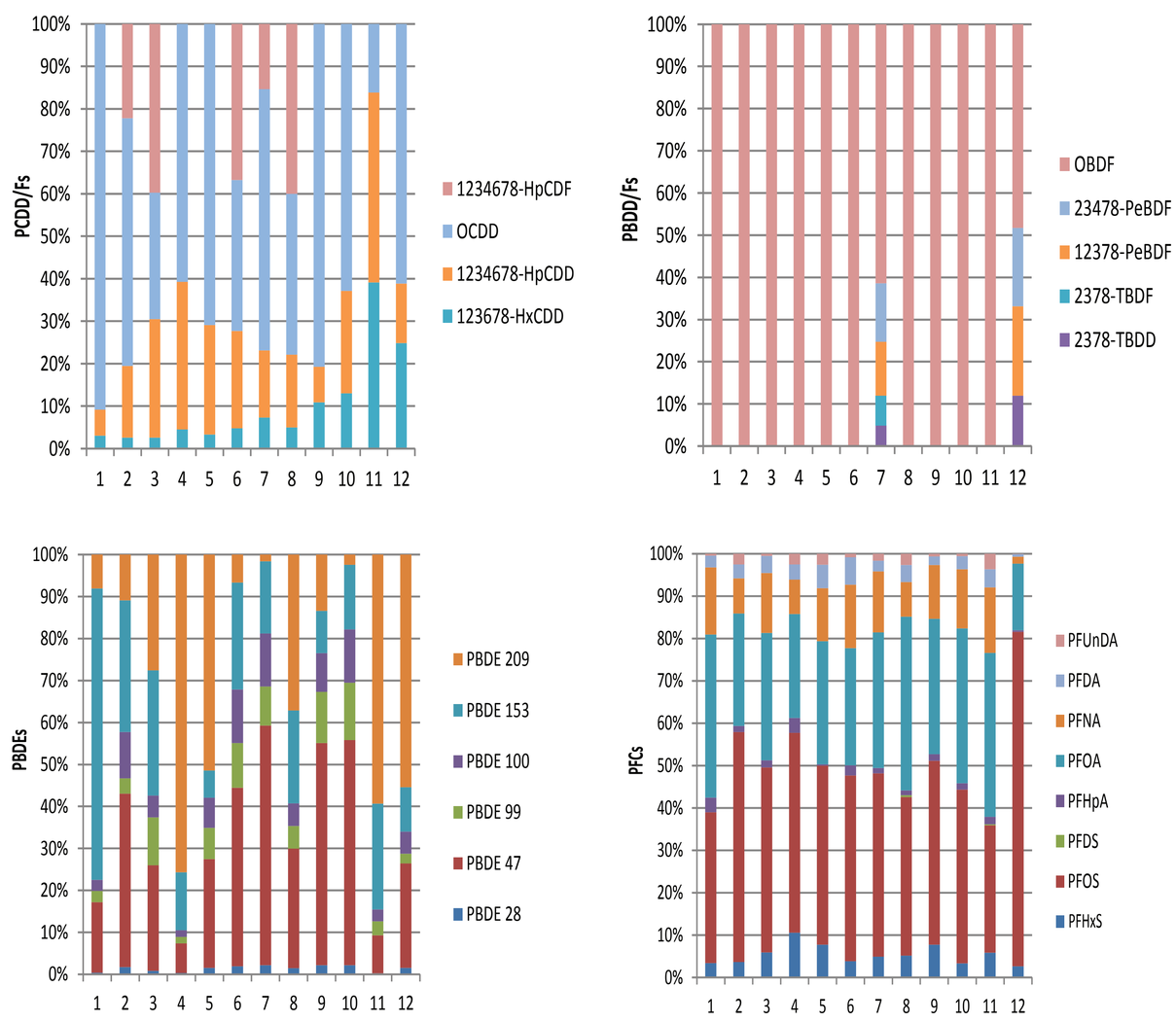

Fig. 1. Congener profiles for PCDD/Fs, PBDD/Fs, PBDEs and PFCs in serum of California firefighters

Conclusions

- This pilot study is the first to report the accumulation of both PCDD/Fs and PBDD/Fs in firefighters following a fire event.
- WHO-TEQs of the PBDD/F concentrations in firefighter blood were 21 times higher than PCDD/F TEQs, suggesting that PBDD/Fs may pose substantial health risks to firefighters.
- The distinctive PBDD/F, PCDD/F, PBDE, and PFC congener patterns found in serum of these firefighters are similar to those reported in other firefighter studies.
- The predominance of of BDE-209 in serum implies continuous exposure to deca-BDE released from burning materials during firefighting.
- The elevated PFOA and PFNA concentrations found in firefighter serum suggest substantial exposure to these chemicals via smoke inhalation during routine firefighting.
- While preliminary, these findings indicate that firefighters may be at risk for cancer and serious health effects from occupational exposure to PBDD/Fs and other toxic chemicals released during fires. A larger study of firefighters is planned.

Marine Environmental Research Institute

P.O. Box 1652, 55 Main Street, Blue Hill, Maine 04614 (207) 374-2135 www.meriresearch.org