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PCDD, PCDF, and PCB exposure in current and former firefighters from Eastern Siberia

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ABSTRACT

The current study examines whether the occupation of firefighting contributes to exposure to polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and dioxin-like polychlorinated biphenyls (PCBs). We compared serum dioxin concentrations and congener profiles of current firefighters ($n = 13$) with those of men who have ceased employment as firefighters ($n = 17$) and with men employed in occupations other than firefighter ($n = 10$). We found that compared to former or non-firefighters, current firefighters have higher levels of dioxins primarily due to the contribution of PCBs and to a lesser extent PCDFs. PCDFs were significantly higher in former firefighters compared to non-firefighters ($p < 0.05$). Comparisons with studies performed by other investigators suggest that local environmental conditions contribute to some of the elevation of PCBs. The congeners 1,2,3,4,6,7,8-heptachlorodibenzodioxin and PCB-114 were significantly higher in current firefighters when compared to former or non-firefighters. Moreover, levels of these congeners were inversely correlated with years since employed as firefighter (Spearman $r = -0.610$, $p = 0.009$ and Spearman $r = -0.53$, $p = 0.03$, respectively). The classes of dioxins show an overall decline with years since employed as firefighters, this decline is most evident with PCDDs (Spearman $r = -0.46$, $p = 0.06$). Together, the combination of evidence supports firefighting as a source of exposure to dioxins.

1. Introduction

During the course of fire suppression, firefighters may be exposed to common toxicants such as benzene, carbon monoxide, formaldehyde, particulate, and polynuclear hydrocarbons (Bolstad-Johnson et al., 2000; Brandt-Rauf et al., 1988) as well as a complex array of uncharacterized products which vary with burn conditions and materials. As a result, over the course of their working life, individual firefighters differ in the array of toxicants they have encountered, the rate at which they were exposed to various toxicants, and the magnitude of exposure they have accumulated. These exposures may contribute to the excess of prostate cancer, testicular cancer, and non-Hodgkin's lymphoma detected in firefighters (IARC, 2010). Among the possible exposures are dioxins, a generic term that encompasses the polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) whose toxicity is mediated by the aryl hydrocarbon receptor (AHR). Dioxins are potent cellular dysregulators which have been extensively studied as carcinogens, developmental toxicants, and endocrine disruptors (White and Birnbaum, 2009).

Dioxins are typically formed when organic materials are burned in the presence of chlorine under high temperature conditions (Vikelsoe and Johansen, 2000). Substantial quantities can be formed during combustion. For instance, the combustion of one kilogram of high molecular weight PVC produces soot containing about 450 μg International Toxic Equivalents (I-TEQ) of PCDDs and PCDFs (Christmann et al., 1989). This quantity exceeds the US male estimated daily intake of 168 pg TEQ (Schecter et al., 2001) by more than 2.7 million-fold.

In contrast to many combustion products, dioxins have long biological half lives which makes it possible to detect cumulative exposures and the impact of events years after their occurrence through the measurement of blood levels. In humans, the half life for 2,3,4,8-tetrachlorodibezo-*p*-dioxin (TCDD) is approximately 7 years and for 2,3,4,7,8-pentachlordibenzodioxin (PeCDD), almost 16 years (Flesch-Janys et al., 1996). The half lives of specific dioxin congeners vary with age, percent body fat, smoking status and breast feeding (Milbrath et al., 2009). Moreover, combustion may produce a distinctive profile of congeners that may be identified

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Table 1
Demographic characteristics of the study participants.

	Current Firefighters	Former Firefighters	Non-firefighters	p[a]
n	13	17	10	
Age, years Mean (min–max)	42 (33–51)	45 (35–54)	45 (38–52)	0.538
BMI, kg/m^2 Mean (min–max)	26.6 (23.3–29.6)	27.4 (21.7–36.0)	25.4 (21.1–30.3)	0.388
Total # disabled	0	14 (3)[b]	0	
# involved in Shelekhov fire	4	16		
Operational experience as firefighters, years	17 (9–29)	14 (9–25)	0	

[a] Significance level (*p*) in intergroup comparison: one-way analysis of variance (Kruskal–Wallis ANOVA).
[b] In parenthesis, the number of the firefighters whose disability is not related to the fire suppression at cable factory in 1992.

in biolipids provided that the biological half life is taken into account.

Although dioxins are known to be formed during combustion processes, little is known about the extent of occupational exposure to firefighters. Firefighters are recognized to be at risk of inhalational exposure to a variety of toxicants but most studies have focused on respiratory function rather than specific exposures. Despite the need for protection, firefighters tend not to use respirators in the absence of visible smoke, a practice that has been shown to lead to inhalation of respirable particulate (Austin et al., 2001). Even when respiratory protection is used, firefighters often show alveolar inflammatory reactions consistent with smoke inhalation (Bergstrom et al., 1997).

The cohort described in this study was assembled to study dioxin exposure and health effects following the 1992 Shelekhov fire which took three days to bring under control. During that event, more than 1000 tons of polyvinylchloride (PVC), polyethylene and other plastics raised concern that firefighters were exposed to dioxin through the inhalation of contaminated smoke. The use of respiratory protection was minimal due to limited access to equipment and concerns about explosion when using compressed oxygen (Chernyak et al., 2004). Klyuev et al. (2001) estimated that the Shelekhov fire produced 22–57 g I-TEQ of PCDD and PCDFs based on analysis of controlled burning of PVC and taking into account the quantities of PVC present in the warehouse.

The purpose of this study is to assess whether firefighters are occupationally exposed to dioxins based on the differences in dioxin concentrations and congener patterns detected between current firefighters, former firefighters and men employed in occupations other than firefighter.

2. Materials and methods

2.1. Selection of the cohort and blood donors

The current study examines dioxin levels in 40 men, thirty of whom were recruited from a cohort of 165 firefighters originally assembled in 2003 to study dioxin exposure and health effects following the 1992 Shelekhov fire (Chernyak et al., 2004). This report includes an additional 10 men who were recruited to serve as non-firefighter controls.

The thirty participants from the original Shelekhov study were grouped according to their status as current or former firefighters. The new control group consists of 10 men who have never worked as firefighters and whose age and body mass indices (BMI) are comparable to those of the Shelekhov study participants (Non-firefighter). The formation of the firefighter groups was complicated due to the limited number and inaccessibility of candidates for a variety of reasons including change of residence and death. Approximately 20 of those contacted declined to participate. All participants are from similar economic strata within Irkutsk Oblast.

Information on demographic, familial, occupational, and personal characteristics including smoking habits, diet, hobbies, and illnesses was obtained through an oral questionnaire. Informed consent which included authorization for blood sampling and banking was provided by all participants. The study protocol was approved by the Biomedical Ethics Committee of East-Siberian Scientific Center of Siberian Branch of Russian Academy of Medical Sciences in Irkutsk and the Brooklyn College-CUNY Institutional Review Board.

2.2. Measurement of serum dioxin concentrations

After overnight fasts, blood samples were collected from 40 individuals in 15 ml red top glass vacutainer tubes. Serum was extracted from the 40–50 ml of whole blood taken from each individual using a standardized procedure. It was then transferred to solvent cleaned glass vials with paperless Teflon-lined screw caps, frozen, and delivered to the lab for analyses. A total of 40 dioxin analyses were performed at the A.N. Severtsov Institute of Ecology and Evolution (Moscow) which is accredited under ISO/IEC 17025:2005. Seven PCDD, 10 PCDF, and 12 PCB congeners (consisting of the non-ortho substituted PCBs, 77, 81, 126, 169, and mono-ortho substituted PCBs 105, 114, 118, 123, 156, 157, 167, 189) were analyzed in each of the samples.

The method for sample preparation, clean up and analysis is described in the Laboratory SOP "Guideline on identification and isomer specific determination of polychlorinated dibenzo-*p*-dioxins, dibenzofurans, biphenyls and organochlorine pesticides in biological samples by HRGC-HRMS", which followed US EPA 1613, 1668, and U.S. Centers for Disease Control and Prevention. Briefly, serum were extracted by hexane: acetone with the addition of ammonium sulfate; the extracts were fractionated to planar (PCDDs, PCDFs and c-PCBs) and non-planar fraction (others PCBs) on carbon columns and further purified on an acid–base silica multilayer and column alumina column. The analyses of both fractions were performed by gas chromatography/high-resolution mass spectrometry using Thermo Finnigan MAT 95XP at resolution 10,000, equipped with a SGE BPX-5 column (30 m × 0.22 mm × 0.25 μm) for planar fraction and SGE HT-8 column (30 m × 0.25 mm × 0.25 μm) for non-planar compounds. Each analytical run consisted of a method blank and four unknown samples. All solvents, sorbents and reusable glassware were tested to ensure the absence of contaminants and interference.

The system of toxicity equivalent factors developed by the World Health Organization (WHO-TEF) in 1998 (for humans) and 2005 were used to calculate total toxicity equivalent (TEQ) (Van den Berg et al., 1998, 2006). Measurements below the limit of detection (LOD) were assigned a value representing the level of detection divided by the square root of 2 (Horning and Reed, 1990). We estimated body burden with TEQ^{98} and the following formula: $\%\text{Lipids} = 495/(1.0324 - 0.19077(\log(\text{waist} - \text{neck})) + 0.15456(\log(\text{height}))) - 450$.

2.3. Statistical analysis

We used Statistica software package (v. 6.1, StatSoft Inc., OK, USA) to perform all statistical analysis. Differences between the three groups were assessed with the Kruskal–Wallis ANOVA and Mann–Whitney *U* non-parametric tests. The Spearman rank correlation test was applied to test for correlation between the concentrations of different congeners and demographic variables. A confidence level of 0.05 was used as the criteria for statistical significance.

3. Results

3.1. Study population

The demographic characteristics of the 40 male participants included in this study are shown in Table 1. Participants were divided into three groups based on employment status as firefighter, specifically Current Firefighters ($n = 13$), Former Firefighters ($n = 17$), and Non-firefighters ($n = 10$). The three groups, selected from a common geographical area and social strata, are of similar ages and have similar BMIs. Among the Former Firefighters, the time elapsed since cessation of employment varied from 2 to 15 years. For 14 out of the 17 Former Firefighters, over 5 years had elapsed by the time of the study. Fourteen of the 17 Former Firefighters are disabled while none of the Current Firefighters have