

## Assessment of serum PCDD, PCDF and PCB levels in firefighters exposed to combustion products during the 1992 "Irkutskcable" factory fire in the city of Shelekhov, Russia

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### Introduction

In December 1992, a fire broke out in a warehouse of the "Irkutskcable" factory in the city of Shelekhov, Russia. Over the next three days, the fire destroyed four additional factory warehouses. The building in which the factory was located was sufficiently large, twelve-meters high, to permit the entry of firefighters and their trucks during the fire. The total area affected by the fire was 16280 m<sup>2</sup>. The rest of the approximately 60000 m<sup>2</sup> building was not damaged. Temperatures exceeding 600° C deformed the roof causing it to collapse with the resultant ignition of the technical and raw materials kept in the shops and storerooms. Combustion products were drawn into the air systems of the shops and immediate environment. The height of the air emissions during the first hours of the fire reached 100 m. The ignition of 250 tons of cable oil made it impossible for the firefighters to use their closed circuit respirators because of the danger of explosion. Only the firefighters of one division were provided with compressed air equipment, and they worked in the most difficult areas. According to existing records, 522 firefighters and 12 individuals from the factory fire department participated in the fire liquidation. Moreover, 230 teaching officers and students from Irkutsk Firefighters School were involved. The fire destroyed about 1000 tons of various raw materials, mainly polyvinylchloride and polyethylene. The firefighters had varying degrees of involvement with the liquidation of the fire, during which they were exposed to a complex mixture of toxic compounds that contained dioxins. An estimated, 22 to 57 g of dioxins (in I-TEQ<sub>DF</sub>) were formed during the fire<sup>1</sup>. Previously, we described the health disorders of this cohort of firefighters in detail<sup>2</sup>. Dioxin toxicity due to the short but intense respiratory exposure could be responsible for the observed health effects. Following is a report of new data examining dioxin levels in 15 "Shelekhov" and 5 control firefighters.

## Materials and Methods

**Selection of the cohort and serum donors:** Twenty of 165 firefighters were selected for dioxin analyses and are examined within the framework of the project “An epidemiological study examining the impact of exposure to combustion products formed during the 1992 “Irkutskcable” fire upon the health of “shelekhov” firefighters”. Using data obtained by the Institute clinic, the firefighters were divided into four groups with five individuals in each group. Group 1 consists of subjects who in 1992-1993 were first taken to the hospital after the fire with symptoms of acute intoxication and a distinctive syndrome characterized by acute distal sensory and autonomic polyneuropathy (Shelekhov syndrome). Group 2 consists of firefighters who had symptoms related to the fire but were registered one to two years later with Shelekhov syndrome. Group 3 includes Shelekhov firefighters that may or may not have had acute intoxication but did not develop Shelekhov syndrome. Group 4 consists of firefighters who did not participate in the Shelekhov fire. Eligible candidates for dioxin analyses were over 35 years old, had weights between the 10<sup>th</sup> and 90<sup>th</sup> percentile for the cohort, and had donated peripheral blood lymphocytes from which an adequate quantity of good quality RNA had been extracted for expression analyses. From the list of eligible candidates, 5 were selected at random and the order of contacting with selected firefighters was strictly followed.

**Serum dioxin quantitation:** 7 polychlorinated dibenzo-p-dioxin (PCDD), 10 polychlorinated dibenzofuran (PCDF), and 12 polychlorinated biphenyl (PCB) congeners were analyzed in serum obtained from peripheral blood in January 2004. After overnight fasts, blood samples were collected from 20 firefighters in 15 ml red top Vacutainer tubes that were  $\frac{3}{4}$  filled. 50-70 ml of blood was taken from each firefighter and the serum was extracted in the same tubes according to a standard procedure. The serum was transferred to glass vials with teflon lined screw caps, frozen, and delivered to the lab for analyses. Congeners were analyzed using the methods developed by the U.S. Centers for Disease Control and Prevention<sup>3,4</sup>. Briefly, the extracts were purified on an acid-base silica multilayer column and rotary evaporated to 2 ml. The extract was transferred to a basic alumina column and a series of elutions using either hexane or a mixture of hexane-dichloromethane were used to separate the PCDD/Fs from the PCBs. The separated fractions were then each cleaned on a carbon column. The analyses of both fractions were performed on GC-HRMS (Hewlett Packard HP 6890 Plus, Finnigan MAT 95XL) at resolution 10000, equipped with a DB-5ms column (20 m length, 0.18 mm id, 0.18  $\mu$ m film thickness, J&W Scientific). 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.

**Data analysis:** Exposure results were reported as TEQ using WHO TEFs<sup>5</sup>. Statistical analysis was performed SPSS 11.5.0. For the exposure data, results below the detection limits were analyzed as “0” values. Exposure variables were log transformed to achieve normality.

## Results and Discussion

**Questionnaire results:** Firefighters were interviewed using a structured questionnaire and the results are presented in Table 1. Seven out twenty of the firefighters are officers with supervisory responsibilities. When asked about their participation during the three days of uncontrolled fire, all but two of the Shelekhov firefighters were present the first initial day of the fire. None of the firefighters in Groups 1 and 2 are currently employed as firefighters while in Group 3, 2 out of the 5 men continue to work as firefighters. Eleven out of the 15 Shelekhov firefighters sought medical

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help immediately after the fire with an additional 3 firefighters seeking medical attention in 1994. An additional firefighter who didn't seek medical help said he felt persistent fatigue after the fire. Although all of the firefighters from Groups 1 and 2 asked for the medical assistance after the fire, those in Group 1 received disability faster than the firefighters from Group 2.

**Table 1:** Questionnaire results

Group	# ID	Questionnaire items						
		Officer	Days at fire	Resp <sup>1</sup>	Fire Start <sup>2</sup>	Fire Stop <sup>3</sup>	Med <sup>4</sup>	Disable <sup>5</sup>
1	100	yes	1, 2, 3	yes	1982	1995	1992	1995
	162	no	1, 2	no	1978	1993	1993	1993
	160	yes	1	no	1972	1994	1992	1993
	60	no	1, 2	yes	1983	1995	1993	1995
	23	no	1	no	1980	1995	1993	1995
2	114	no	1, 2	no	1986	1995	1993	1995
	39	no	3	yes	1982	2000	1994	2000
	4	yes	1, 2	no	1977	1995	1992	1996
	111	no	1	no	1983	1999	1993	1999
	31	yes	1, 3	no	1976	1996	1992	1996
3	71	no	1	no	1992	no	no	no
	150	no	1	no	1984	1998	1993	2002
	143	yes	1, 2	no	1977	1999	1994	no
	33	no	2, 3	no	1992	2003	1994	no
	73	no	1	no	1992	no	1993	no
4	156	no	0	-	1995	no	no	no
	152	yes	0	-	1993	no	no	no
	38	yes	0	-	1973	no	no	no
	157	no	0	-	1995	no	no	no
	51	no	0	-	1988	no	no	no

<sup>1</sup>Respirator was used

<sup>2</sup>First year as a firefighter

<sup>3</sup>Last year as a firefighter

<sup>4</sup>Year of Shelekhov-related medical assistance

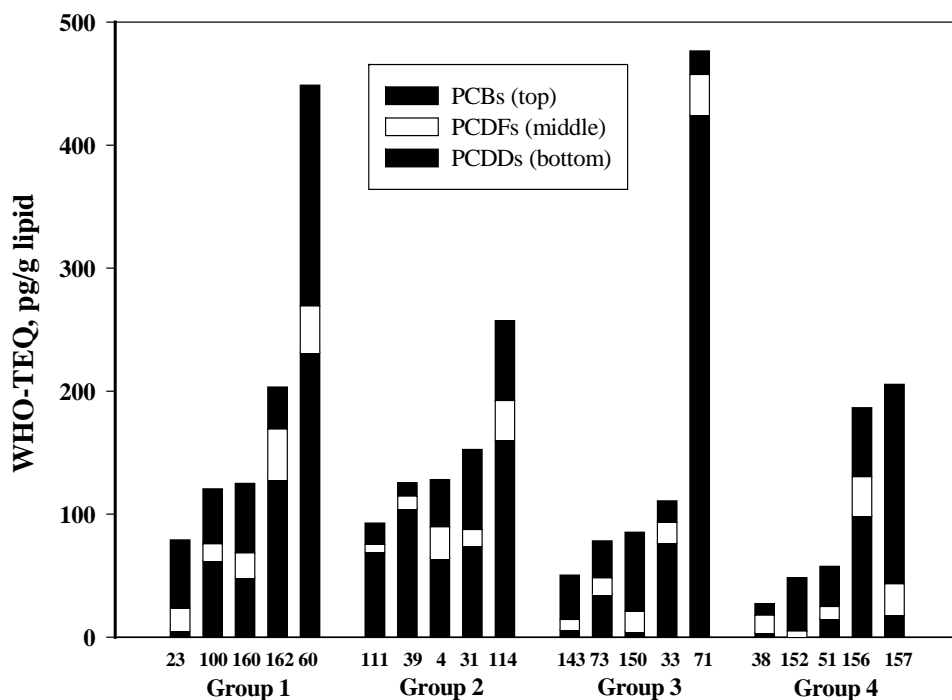
<sup>5</sup>Year declared to be disabled

**Dioxin exposure:** Figure 1 shows the relative contribution of PCDDs, PCDFs and PCBs for each firefighter. Overall, the Total TEQs measured in this cohort are quite high. Out of twenty firefighters, 11 have Total TEQs exceeding 100 pg/g lipid. Of these, 5 have Total TEQs exceeding 200 pg/g lipid and 2 exceed 400 pg/g lipid. Two Group 4 controls, currently working as firefighters have Total TEQs that exceed 200 pg/g lipid indicating that high levels of exposure occur in non-Shelekhov firefighters and that high TEQ levels do not preclude employment. Indeed, a firefighter in Group 3 (ID71) had the highest measured Total TEQ of 477 pg/g lipid and continues to work. There was considerable variability in the measured Total TEQs. For instance, ID71 and ID73, from the same firefighter unit, worked together during the Shelekhov fire, yet their Total TEQ differs by 6-fold.

**Dioxin exposure correlates:** Table 2 examines the relationship between selected variables and serum dioxin levels among the firefighters. As mentioned earlier, the groups were formed on the basis of whether they developed Shelekhov syndrome. Group 1 exhibited the syndrome immediately after the fire whereas Group 2 exhibited the syndrome after a delay of 1-2 years.

Group 3 consists of firefighters that participated in the Shelekhov fire but did not develop the syndrome and Group 4 are control firefighters who did not participate in the fire. The four groups did not differ in age, BMI, or years worked. Their dioxin exposures, whether measured as TCDD or as PCDDs, PCDFs, PCBs, or Total TEQ also did not differ. Although Group 1 exposures were not

significantly higher than those of other groups, it should be noted that none of them have worked as firefighters since 1993 to 1995, approximately 10 years ago.



**Figure 1:** Serum concentrations of PCDDs, PCDFs and PCBs

Comparison of the Shelekhov firefighters (Groups 1-3) with the controls shows that they had significantly higher levels of exposure to PCDDs ( $p=0.03$ ). Comparison on the basis of the Shelekhov syndrome (Groups 1 and 2) with Shelekhov firefighters without the syndrome (Group 3) or Group 4 controls indicated that PCDD exposure varied non-significantly between the comparison groups ( $p=0.07$  ANOVA) although post-hoc comparisons did not indicate significant differences.

Stratification of the cohort on “days at fire” suggests that firefighters who participated in the Shelekhov fire for 2-3 days had exposures that resembled firefighters who participated for only one day. In addition, firefighters using respiratory protection had significantly higher PCDD exposures than those that did not, possibly because they tended to enter smokier areas. However, only three firefighters used respirators so this result should be interpreted with caution.

“Rank” was associated with exposure with officers having lower serum concentrations of TCDD, PCDDs, PCDFs, PCBs and Total TEQs. The results for Total TEQs neared significance with  $p=.070$ . Whether the differences between officers and non-officers are due

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**Table 2.** Demographic variables and TCDDs, PCDDs, PCDFs and PCBs in firefighter

	n	Age, yr <sup>1</sup>	BMI <sup>1</sup>	Yrs <sup>1,4</sup>	TCDD <sup>1,2</sup>	PCDD <sup>1,2</sup>	PCDF <sup>1,2</sup>	PCBs <sup>1,2</sup>	TOTAL <sup>2,3</sup>	
Group	1	5	48.0 (6.1)	26.5 (2.7)	15 (4)	62 (62)	95 (88)	26 (12)	74 (60)	195 (79, 449)
		5	42.3 (2.8)	29.0 (3.5)	16 (4)	40 (17)	94 (40)	18 (11)	39 (26)	151 (93,257)
	3	5	43.3 (4.5)	25.4 (3.1)	14 (5)	52 (80)	109 (179)	18 (9)	33 (19)	160 (50, 477)
		5	42.2 (5.8)	25.6 (2.6)	14 (9)	13 (15)	27 (41)	17 (11)	61 (59)	105 (27, 205)
Shelekhov vs control	1-3	15	44.5 (5.0)	27.0 (3.3)	15 (4)	51 (56)	<b>100<sup>8</sup></b> ( <b>109</b> )	20 (11)	49 (41)	169 (50, 477)
		5	42.2 (5.8)	25.6 (2.6)	14 (9)	13 (15)	<b>27 (41)</b>	17 (11)	61 (59)	105 (27, 205)
	1-2	10	45.1 (5.4)	27.7 (3.2)	16 (4)	51 (44)	<b>95<sup>6</sup></b> ( <b>64</b> )	22 (12)	57 (47)	173 (79, 449)
Shelekhov Syndrome vs without	3	5	43.3 (4.5)	25.4 (3.1)	14 (5)	52 (80)	<b>109</b> ( <b>179</b> )	18 (9)	33 (19)	160 (50, 477)
		5	42.2 (5.8)	25.6 (2.6)	14 (9)	13 (15)	<b>27</b> ( <b>41</b> )	17 (11)	61 (59)	105 (27, 205)
	2-3	8	46.0 (5.9)	27.1 (4.1)	15 (5)	57 (48)	<b>100</b> ( <b>70</b> )	24 (12)	60 (51)	184 (50, 449)
Days at Fire	0	5	42.2 (5.8)	25.6 (2.6)	14 (9)	13 (15)	<b>27<sup>7</sup></b> ( <b>41</b> )	17 (11)	61 (59)	105 (27, 205)
		7	42.8 (3.4)	26.8 (2.4)	15 (4)	45 (67)	<b>99</b> ( <b>148</b> )	17 (9)	36 (22)	152 (78, 477)
	2-3	8	46.0 (5.9)	27.1 (4.1)	15 (5)	57 (48)	<b>100</b> ( <b>70</b> )	24 (12)	60 (51)	184 (50, 449)
Respiratory protection	No	17	43.7 (4.9)	<b>26.1</b> ( <b>3.1</b> )	15 (6)	36 (47)	<b>72<sup>8</sup></b> ( <b>102</b> )	19 (10)	47 (36)	139 (27, 477)
		3	45.2 (7.4)	<b>29.5</b> ( <b>1.2</b> )	14 (3)	72 (76)	<b>133</b> ( <b>88</b> )	21 (15)	78 (89)	232 (121, 449)
	Yes	3	44.5 (5.0)	25.9 (4.5)	19 (7)	22 (20)	37 (32)	14 (7)	42 (18)	<b>93<sup>6</sup></b> ( <b>27, 153</b> )
Rank	High	7	43.7 (5.4)	27.0 (2.3)	13 (3)	52 (60)	105 (117)	22 (12)	57 (54)	<b>185</b> ( <b>57, 477</b> )
		13	42.7 (5.2)	<b>25.1<sup>8</sup></b> ( <b>2.5</b> )	14 (7)	36 (61)	75 (135)	18 (10)	45 (46)	138 (27, 477)
	Low	13	44.9 (5.1)	<b>27.8</b> ( <b>3.1</b> )	16 (4)	46 (44)	87 (67)	21 (11)	57 (45)	165 (79, 449)
Disability	No	9	45.3 (4.9)	27.3 (3.4)	16 (4)	43 (42)	80 (65)	20 (11)	53 (42)	152 (50, 449)
		13	41.4 (4.9)	25.3 (2.2)	13 (8)	40 (68)	85 (153)	19 (11)	50 (52)	154 (27, 477)
	Yes	7	45.3 (4.9)	27.3 (2.2)	13 (8)	40 (68)	85 (153)	19 (11)	50 (52)	154 (27, 477)
Working <sup>5</sup>	No	13	41.4 (4.9)	25.3 (2.2)	13 (8)	40 (68)	85 (153)	19 (11)	50 (52)	154 (27, 477)
		7	45.3 (4.9)	27.3 (2.2)	13 (8)	40 (68)	85 (153)	19 (11)	50 (52)	154 (27, 477)

<sup>1</sup> arithmetic mean (SD)

<sup>2</sup> WHO-TEQ pg/g lipids; log transformed data

<sup>3</sup> (low value, high value)

<sup>4</sup> Yrs, Years employed as a firefighter

<sup>5</sup> Currently working as a firefighter

<sup>6</sup> p=0.070 ANOVA

<sup>7</sup> p<0.10 and p > 0.05 t test

<sup>8</sup> p<0.05 t test

to conditions encountered during the Shelekhov fire or due to the cumulative effects of different responsibilities in general cannot be ascertained due to the small numbers. However, the earlier observation that the Shelekhov fire is associated specifically with exposure to PCDDs rather than the elevated PCDFs or PCBs observed in the non-officers suggests that the difference is not related to the Shelekhov fire but is characteristic of all firefighters. Disabled firefighters had dioxin exposures similar to firefighters that were not disabled although they did differ by having significantly higher BMIs. The exposure of firefighters who are currently working does not differ from those who are not working.

As a group, the firefighters survey had a total mean arithmetic TEQ of 153 pg/g lipid, with a median of 123 pg/g. The 95% confidence interval for this cohort was from 96 to 210 pg/g. These values exceed those seen with typical environmental exposures and with environmental contamination<sup>6</sup> but have been noted in occupationally exposed populations<sup>7</sup>. The observed results may be due to exposures sustained during firefighting or from environmental sources. However, firefighting in general appears to be a major contributor as evidenced by the trend for higher PCDF and PCB exposures seen among the lower ranking firefighters. Involvement with the Shelekhov fire appeared to result in greater exposures to PCDDs. Over 11 years have elapsed and so the contribution of the Shelekhov fire may no longer be pronounced due to the decline of serum levels. Given the limitations posed by the small number of study participants, we conclude that this is a population with significant dioxin exposure and that the relationship between biomarkers and the health impact needs to be examined.

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