

## **FIRES AT CHEMICAL PLANTS. ARE FIREMEN A DIOXIN EXPOSURE RISK GROUP?**

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### **Introduction**

According to statistical data fires at industrial enterprises make no less than 2% of the total number of fires. This means that annually there occur about 150000 large fires (more than 17 fires per hour) in the world. These fires cause maximum social, economical and environmental damage.

Especially great damage to human health is caused by fires at chemistry and oil chemistry plants due to emission into the atmosphere of great amounts of toxicants including PCDD/Fs and PCBs what makes them a probable source of pathological changes, genetic disturbances, chronic occupational diseases from which firemen suffer.

In order to study possibilities of probable occupational PCDD/Fs and PCBs exposure 2 groups of firemen were examined who participated in extinguishing numerous fires at chemical and oil refining plants in Ufa and Shelekhovo, Russia.

### **Objects and Methods**

**A group of firemen from Shelekhovo.** A fire at a plant producing cables in the city of Shelekhovo, Irkutsk Region, in 1992 that was accompanied by burning of more than 600 cubic meters of PVC for 10 days was disastrous to the health of about 400 firemen. The majority of them are invalids now. This group was under medical control that included PCDD/Fs and coplanar PCBs determination in donor blood at several laboratories<sup>1,2,3</sup>. For 28 firemen PCDD/Fs and DLPCBs WHO levels were determined in two independent research works<sup>3,4</sup>. In 2002 one more study of representatives of this group of firemen in Shelekhovo was carried out. Whole blood samples were taken from 15 firemen, 5 of them had already participated in the research, for the rest of them PCDD/Fs and DLPCBs exposure level was determined for the first time. Every person gave 35-45 ml of blood. The mean age of the donor group was 45 years old.

**A group of firemen from Ufa.** The ground for forming a group of firemen was their participation in extinguishing large fires at chemical and oil chemical plants in Ufa for 10-15 years including the fire at Chimprom plant polluted with PCDD/Fs due to 2,4,5-T production. Characteristics of pollution levels and consequences of workers exposure were discussed in detail in previous publications<sup>5,6,7</sup>.

In Ufa there are largest refineries and chemical plants where great fires and emergencies occurred resulting in burning of oil products (9) and reaction mixtures. The largest of them took place in 1990 at the chemical plant as a result of a reactor explosion where reaction mass contained isopropyl benzene, acetone, phenol and hydroperoxide compounds and 8-hour fire followed. In the process of the fire extinguishing there were conditions for acute and chronic intoxication by chemicals of more than 150 firemen. In 1992 as a result of explosion at a shop where 2,4,5-T had earlier been produced (the material of the building is still polluted with PCDD/Fs up to 10-12 ppb TEQ)<sup>5</sup> for the same people there was a chance to be exposed to PCDD/Fs products of burning and

dust. The group of firemen in Ufa consisted of 38 people whose blood plasma was analyzed individually. The mean age of the group was 39.5 years old.

Individual blood and plasma samples of 45 and 15 ml in volume respectively were frozen at  $-20^{\circ}\text{C}$  and kept until analyzing. Standard solutions  $\text{C}^{13}$  – PCDD/Fs (CIL, EDF 8999-4) and  $\text{C}^{13}$  – PCBs (Wellington) were introduced into the samples. Extraction of the plasma sample was made by the mixture of ethyl ether-hexane, the whole blood sample was extracted by the mixture of methylene chloride-hexane-ethyl ether. The extract was purified from lipids, proteins, steroids with the use of a preparation column Envirogel TM GPC Cleanup (Waters) separating the fractions containing PCDD/Fs and PCBs.

Registration and measurement were carried out in compliance with the Methods US EPA 1613 and 1668 using the measurement system Autospec-Ultima (10000), DB-5 MS, 60m. The recovery was 57-95% depending on PCDD/Fs isomer and 83-100% for PCBs.

### Results and discussion

The results of PCDD/Fs and PCBs-WHO determination for both groups of firemen are given in Tables 1 and 2. The mean level of PCDD/Fs and PCBs exposure determined for donors from Shelekhovo in this research is close to our previous results<sup>3</sup>. We also did not find any considerably increased levels both of PCDD/Fs and DLPCBs as compared with the data reported for the population of the city (TEQ PCDD/Fs –14,5 pg/g lipids and TEQ PCBs-WHO -37,9 pg/g lipids of whole blood)<sup>4</sup>.

Table 1

**PCDD/Fs and DLPCBs in blood and serum samples, pg/g lipids**

PCDD/Fs	Shelekhovo, n=15			Ufa, n=36		
	Min-max	mediana	mean	Min-Max	mediana	mean
2378-TCDD	1.8-6.7	3.9	4.04	1,7-25.3	4.4	7.7
12378-PnCDD	1.8-8.3	6.4	5.8	2,3-22.9	7.1	9.4
123478-HxCDD	0.9-14.3	4.1	5.5	3,4-66.2	8.2	12.4
123678-HxCDD	1.9-21.2	6	7.6	3,4-47.4	10.7	13.2
123789-HxCDD	0.9-17.7	3.9	5.6	ND (1)- 36.7	7.3	11.9
123678-HpCDD	7.3-73.1	19.9	28.2	4.2-70.0	21.4	25.7
OCDD	52.9-476.8	127.0	162.6	71.2-555.3	233.3	271.5
2378-TCDF	0.8-15.8	2.6	4.0	2.1-27.3	4.5	6.7
12378-PnCDF	0.6-12.1	2.2	3.4	0.7-9.0	4.2	4.6
23478-PnCDF	1.6-16.8	10	9.9	2.9-22.7	9.2	10.1
123478-HxCDF	1.5-12.6	6.4	7.2	1.7-39.4	4.9	9.7
123678-HxCDF	0.8-15.1	6.2	6.4	1.6-32.0	5.2	6.8
123789-HxCDF	0.9-16.8	4.3	5.6	1.8-21.8	5.2	8.2
234678-HxCDF	0.8-8.9	3.3	4.0	ND(1)- 24.1	5.9	6.9
1234678-HpCDF	1.1-70.1	15.2	15.7	2.8-36.3	8.8	11.1
1234789-HpCDF	0.8-41.4	10.3	11.2	0.3-59.4	6.2	11.6
OCDF	1.1-19.9	4.1	5.1	0.7-15.7	6.4	6.9
<b>TEQ-WHO PCDD/Fs</b>	<b>12.6-31,8</b>	<b>20.5</b>	<b>20.2</b>	<b>12.1-53.5</b>	<b>25.0</b>	<b>29.2</b>

PCDD/Fs level in plasma of firemen from Ufa also does not differ from the control group of Ufa people - 27.6 pg/g lipids TEQ<sup>8</sup>. The control group consisted of 15 men, mean age was 38 ± 2 years old. TEQ DLPCBs in blood of Ufa citizens is 8,1 pg/g lipids of serum for the age group of 20 years old (n=9) and 14,9 pg/g lipids for 40 years old(n=4).

When comparing generalized results for two groups it becomes obvious that PCDD/Fs level in Ufa exceeds that of Siberian firemen, and on the contrary, PCBs prevail in blood of firemen from Shelekhovo.

The reasons for this difference are evidently accounted for by local living conditions because the same regularities are found for the population of both cities.

Comparing the data on PCBs in blood of people, workers and firemen from two geographically distant regions we may suppose that Irkutsk region in Siberia is more polluted by PCBs in comparison with Bashkortostan, South Ural, probably due to local industrial emissions.

We did not find any convincing proofs of increased occupational risk of PCDD/Fs and PCBs exposure of firemen even in case of great and longtime fires at chemical and oil chemical plants apparently because of a short period of exposure and the use of protection facilities.

Table 2

**DLPCBs in blood and serum from Shelekhovo and Ufa, ng/g lipids (TEQ-WHO pg/g lipids)**

DLPCBs, ng/g lipids	Shelekhovo, n=15			Ufa, n=36		
	Min-max	mediana	mean	Min-Max	mediana	mean
33'44'-TCB(77)	ND-0,4	0,04	0,09	0,04-0,7	0,3	0,3
344'5'-TCB(81)	ND-0,8	0,01	0,1	ND-0,2	0,04	0,06
233'44'-PnCB(105)	2,1-31,7	8,9	11,6	1,8-20,1	8,7	8,9
2344'5'-PnCB(114)	1,0-5,8	2,2	2,4	0,4-2,8	1,4	1,5
23'44'5'-PnCB(118)	2,1-7,7	25,6	35,2	3,7-57,2	25,9	27,5
2'345'5'-PnCB(123)	ND-0,6	0,2	0,2	ND- 1,7	0,6	0,6
33'44'5'-PnCB(126)	ND-0,1	0,06	0,06	ND-0,2	0,002	0,02
233'44'5'-HxCB(156)	9,7-38,9	17,9	18,8	1,9-20,4	7,6	8,7
233'44'5'-HxCB(157)	1,5-9,1	2,7	3,6	0,5-5,6	1,9	2,2
23'44'55'-HxCB(167)	0,6-4,8	2,7	2,5	0,5-4,2	1,8	2,0
33'44'55'-HxCB(169)	ND-0,1	0,06	0,06	ND-0,06	0,02	0,02
233'44'55'-HpCB(189)	0,5-5,8	1,6	1,8	0,1-1,28	0,5	0,6
<b>TEQ DLPCBs, pg/g lipids</b>	<b>14.2-37.3</b>	<b>22.6</b>	<b>23.3</b>	<b>5.9-74.4</b>	<b>14.0</b>	<b>19.7</b>

For 5 donors of Shelekhovo cohort there is a possibility to compare the found results with earlier published data<sup>3,4</sup>.

**Table 3. 2,3,7,8-TCDD and TEQ in blood samples of firemen from Shelekhovo in 5, 7 and 9 years after the exposure (pg/g lipids of blood)**

Donors	2,3,7,8-TCDD	TEQ PCDDs	TEQ PCDFs	TEQ DLPCBs	Source
#1, 1998	7.8	18.1	22.4	NA	[1]
#1, 2000	5.9	15.6	16.1	29.9	[3]
#1, 2002	5.1	14.4	9.5	25.6	Given report
#2, 1998	1.0	2.9	4.4	7.6(##77,126,169)	[2]
#2, 2000	3.1	13.3	7.58	20.9	[3]
#2, 2002	2.6	8.7	7.2	20.6	Given report
#3, 1998	7.5	22.9	13.2	NA	[2]
#3, 2000	5.8	17.8	7.15	39.6	[3]
#3, 2002	6.1	18.6	5.4	13.9	Given report
#4, 2000	4.0	23.4	6.52	21.3	[2]
#4, 2002	4.3	13.2	5.3	16.3	Given report
#5, 2000	2.3	22.1	8.8	19.1	[3]
#5, 2002	2.1	10.3	3.0	14.3	Given report

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