

# HUMAN EXPOSURE I –POSTER

## COHORT OF FIREMEN, SHELEKHOVO, RUSSIA. PCDD/Fs, PCBs AND PBDEs IN BLOOD LIPIDS

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### Introduction

In view of the fact that formation of dioxin-type compounds most probably occurs in thermal processes determination of these compounds content in blood of firemen donors who suffered as a result of the impact of combustion materials is of special interest when studying accident consequences in Shelekhovo (a fire at a cable plant in December, 1992).

Studying the impact on donors' organism was carried out during the 2<sup>nd</sup> stage of a Russian-American project in 1998 by three laboratories –Health Canada (Ottawa), Ergo Fors. (Hamburg) and BREC (Ufa) [1, 2]. No sufficient differences were found in PCDD/Fs and PCBs levels between firemen donors and the background level of urban residents in Irkutskaya region where the suffered were living. Thus for citizens of Angarsk TEQ/WHO PCDD/Fs was 14.8 pg/g lipids (n=1), for Sayansk – 27.7 pg/g lipids (pool, n=11), for Irkutsk – 24.0 pg/g, Baikalsk – 20.0 pg/g lipids (n= 8). The sum of non-ortho-coplanar PCBs (##77, 126, 169) made from 8.8 up to 20 pg/g lipids of blood.

In blood of firemen PCDD/Fs were found at a level of 25.9 pg/g lipids (mean of 17 individual samples). The content of non-ortho-coplanar PCBs was 6 pg/g lipids. PCDD/Fs content in 2 pool samples from 7 and 6 firemen was 30.0 and 24.8 pg/g lipids respectively.

Study of PCDD/Fs and PCBs in fat tissue samples of people living in Irkutskaya region and in the city of Irkutsk and also of the firemen suffered as a result of fire fighting also did not show any sufficient differences. The values were 43, 47 and 53 pg/g lipids respectively (I-TEQ,  $\Sigma$  PCDD/Fs, PCBs) [3]. Samples were taken in 1997, 5 years after the fire, from individual residents of cities in Irkutskaya region and from 9 firemen. The ratio of WHO-TEQ(PCBs)/I-TEQ (PCDD/Fs) was respectively: for Irkutskaya region 1.19 (19.2/22.9); for the city of Irkutsk – 0.88 (26/22) and for the firemen 1.05 (26.3/26.4). Prevailing compounds were determined: OCDD, 2,3,4,7,8-PnCDF, 1,2,3,4,7,8-HxCDF and 1,2,3,6,7,8-HxCDF. When determining PCBs the following were selected as analyzed components: ## 28, 52, 77, 99, 101, 105, 118, 126, 138, 153, 156, 169, 170, 180, 199, 202, 209.

This research is a continuation of the earlier works on the assessment of pollution level but the number of the examined donors and the number of analyzed components has been increased. Assessment of the content of polybrominated biphenyls and diphenyl ethers in blood has been made as a possible effect of exposure due to burning of more than 1000 tons of PVC-containing materials and probable application of bromine - containing fire-extinguishing agents.

### Methods and Materials

HRGC/HRMS analysis of PCDD/Fs was carried out by the method of US EPA 1613 rev. B, determination of DLPCBs – by the method of US EPA 1668 rev. A (labelled surrogates of

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Wellington Lab, calibration solutions, native PCBs, standard extractions  $^{13}\text{C}_{12}$ -PCB ## 52, 101, 138, 178, 209 and purification of PCBs ## 81, 111, CIL).

For examination 25 individual samples of whole donor blood (about 50 ml each) were frozen and kept till the moment of analyzing. The method of sample preparation was described earlier [4]. Separation of mono- and di-ortho-PCBs from PCDD/Fs and non-ortho-coplanar PCBs was carried out by withdrawal of some fractions on a column with alumina. PCDD/Fs and PCBs # 77, 126, 169 were separated by additional fractionating on a carbon column. A measuring system Carlo Erba 8035 – Autospec-Ultima (10.000) with DB-5MS J&W, 60m column was used. Analysis was carried out by batches consisting of 7 samples each. In order to exclude background pollution and to confirm control over the whole analytical system blank tests were carried out. TEQ-WHO scale was used. PBDEs determination was carried out by [5].

## Results and Discussion

Relative distribution of PCDD/Fs and PCBs in blood samples in TEQ units is given in table 1. The content of non-ortho-coplanar PCBs (# 77, 126, 169) makes from 10 to 25% of the total content of all DLPCBs.

**Table 1. WHO-TEQ PCDDs, PCDFs and DLPCBs in donor blood samples, pg/g lipids**

Donor code	PCDDs	PCDFs	PCDD/Fs	PCBs	$\Sigma$ PCDD/Fs, PCBs
A-1	26.3	17.6	43.9	25.6	69.5
A-2	4.9	9.1	14.0	17.5	31.5
A-3	6.6	9.5	16.1	24.9	41.0
A-4	13.3	7.6	20.9	18.6	39.5
A-5	15.5	16.1	31.6	29.9	61.5
A-6	12.3	9.2	21.5	19.6	41.1
A-7	27.7	8.4	36.1	25.3	64.1
A-8	22.9	18.3	41.2	26.0	67.2
A-9	20.2	7.5	27.7	23.8	51.5
A-10	23.4	6.5	29.9	21.3	51.2
A-11	12.6	12.2	24.8	40.2	65.0
A-12	7.3	5.7	13.0	60.0	73.0
A-15	24.5	15.8	40.3	24.2	64.5
A-16	13.9	6.4	20.3	45.6	65.9
A-17	17.8	7.2	25.0	39.6	64.6
A-18	32.9	29.9	62.8	35.9	98.7
A-19	13.8	7.7	21.5	22.6	44.1
A-20	22.2	11.9	34.1	17.0	51.1
A-21	22.1	8.8	30.9	19.1	50.0
A-22	12.7	13.4	26.1	23.9	50.0
A-23	15.4	12.5	27.9	27.8	55.7
A-24	17.9	9.9	27.8	30.9	58.7
A-25	17.5	6.2	23.7	35.7	59.4
A-27	11.4	12.6	24.0	26.3	50.3
A-30	13.3	6.8	20.1	20.4	40.5

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Table 2 PCDD/Fs and DLPCBs in blood(n=25), pg/g lipids

PCDD/Fs, PCBs	Min	Max	Mediana	Mean	Stand. Dev.
2378-TCDD	0.7	9.8	5.2	4.7	2.2
12378-PnCDD	0.7	17.1	6.5	7.4	3.5
123478-HxCDD	2.2	35.8	10.5	12.0	8.8
123678-HxCDD	2.1	51.9	14.8	16.6	11.7
123789-HxCDD	1.2	59.5	10.0	16.1	14.2
123678-HpCDD	12.6	130.7	30.5	35.8	24.8
OCDD	42.7	648.7	246.1	221.8	147.1
2378-TCDF	0.9	22.6	5.1	5.6	4.7
12378-PnCDF	0.8	40.4	2.5	5.1	7.7
23478-PnCDF	1.7	25.2	9.2	9.4	6.6
123478-HxCDF	4.2	61.1	16.1	21.2	13.6
123678-HxCDF	3.3	70.6	11.5	14.2	13.9
123789-HxCDF	1.0	19.2	5.7	6.2	4.7
234678-HxCDF	1.9	52.7	6.0	10.1	11.4
1234678-HpCDF	2.0	96.6	18.9	25.2	22.1
1234789-HpCDF	1.4	29.8	7.2	9.7	7.6
OCDF	17.0	204.8	81.0	80.3	46.6
33'44'-TCB(77)	8.0	89.7	32.0	34.0	21.8
344'5-TCB(81)	6.0	99.2	39.0	40.0	25.5
233'44'-PnCB(105)	838.8	45226.1	4863.5	8404.5	9912.5
2344'5-PnCB(114)	898.6	8523.4	1591.2	2245.3	1784.9
23'44'5-PnCB(118)	16900.0	73170.7	30517.9	31028.5	12472.3
2'345'5-PnCB(123)	53.0	2323.9	486.6	519.5	417.1
33'44'5-PnCB(126)	34.4	138.6	68.1	71.1	27.3
233'44'5-HxCB(156)	12787.4	41481.2	22676.1	23886.1	7516.0
233'44'5-HxCB(157)	1056.3	8543.7	2907.7	3322.7	1881.9
23'44'55-HxCB(167)	2376.3	12374.1	4742.4	5262.3	2136.4
33'44'55'-HxCB(169)	50.1	375.5	96.0	114.6	70.1
233'44'55'-HpCB(189)	761.8	2269.3	1415.3	1416.6	468.1
TEQ-WHO PCDD/Fs	12.9	62.8	26.1	28.1	10.8
TEQ PCB	17.0	45.6	25.3	27.2	7.7
TEQ, total	31.5	98.6	52.1	55.2	13.5
Σ(77, 126, 169)	4.0	15.0	7.8	8.3	2.7

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For 3 firemen changes of PCDD/Fs concentration in blood were traced from 1998 to 2000. There was some increase of octachlorinated isomers and some reduction of tetra- and penta-isomers (Table 3).

**Table 3. PCDD/Fs in blood samples of 3 firemen in 1998 and 2000, pg/g lipids**

PCDD/Fs	A-5		A-17		A-16	
	1998	2000	1998	2000	1998	2000
V, ml	35	43	40	48	30	46
Lip, g	0.116	0.117	0.111	0.126	0.109	0.199
2378-TCDD	7.8	5.9	7.5	5.8	5.5	5.3
12378-PeCDD	5.6	6.3	11.3	6.5	8.9	4.0
123478-HxCDD	2.5	7.6	ND (3)	12.1	4.3	10.5
123678-HxCDD	11.8	14.8	ND (3)	17.9	10.3	16.4
123789-HxCDD	2.2	9.1	ND (3)	22.1	2.3	15.7
1234678-HpCDD	37.3	15.2	26.3	23.8	27.2	24.8
OCDD	129.6	284.0	123.2	246.1	91.5	123.4
2378-TCDF	25.4	1.9	ND (4)	11.9	22.5	11.1
12378-PeCDF	6.9	5.4	9.01	2.2	11.9	2.4
23478-PeCDF	32.2	25.2	31.2	2.1	30.7	2.3
123478-HxCDF	24.5	6.6	23.1	22.2	20.5	11.5
123678-HxCDF	15.3	7.4	10.5	13.6	12.4	13.3
123789-HxCDF	7.5	5.7	ND (2)	3.0	5.7	5.0
234678-HxCDF	13.9	6.0	6.9	8.3	11.9	8.5
1234678-HpCDF	37.3	20.9	23.3	6.4	25.7	15.9
1234789-HpCDF	3.9	28.0	ND (2.6)	4.9	5.0	5.6
OCDF	27.6	115.9	20.5	84.4	19.2	51.9
TEQ - WHO	39.2	31.7	35.4	24.9	39.9	20.3

**Table 4. Concentration of dibromdiphenyl ether isomers in donor blood samples**

Donor code	DBrDE, ng/g lipids	Donor code	DBrDE, ng/g lipids
A-10	121,6	A-18	83,0
A-15	70,2	A-20	107,7
A-16	131,0	A-21	106,5

The content of polybrominated biphenyls in blood samples is at a level of 20-50 pg/g blood lipids. The content of tetra-deca-brominated biphenyl ethers is at the same level.

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