

Dioxin and dibenzofuran levels in the blood of the workers 28 years after occupational exposure to dioxin-dangerous 2,4,5-T.

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1. Introduction

During 1965-1967 the 2,4,5-T production was functioning in Ufa (Russia). In these years more than 200 workers (practically all the workers of the factory department) were diagnosed with chloracne.

Until 1988 2,4,5-trichlorophenol and cuprous 2,4,5-trichlorophenolate were produced at that factory. Up to now the 2,4-D production is functioning, the capacity of which is estimated to be 40000 t/y. Since 1992 this capacity was declined in half.

In 1992 A. Schecter has investigated the PCDD/PCDF and PCBs levels in the blood of Ufa townpeople, nowadays and former workers of that factory (male and female), as well as of the children of the occupationally exposed women ¹⁾.

The blood analysis of the workers has demonstrated the elevated (up to 10 times) content of 2,3,7,8-TCDD in comparison with the background levels in Ufa and some others locations of Russia. The content of other PCDD and PCDF congeners was 2-3 times that of the background levels.

This report represents the analysis results of the whole blood samples of three workers 28 years after occupational exposure to 2,4,5-T production.

2. Materials and Methods

The whole blood samples (25 ml) were kept frozen until analyzing.

We have completely reproduced the analytical technique of sample preparing developed by Patterson D. et al. ²⁾ and modified by Schrey P., Wittsiepe Y. et al. ³⁾, for the analyzing the whole blood samples.

The diluted sample of the whole blood was spiked with 100 ml of internal standard solution, containing sixteen ¹³C₁₂-labelled PCDD/Fs isomers. After the treating with ammonium sulphate and ethanol the sample was extracted with hexane. The fat content in the sample was determined. The extract clean up was performed by standard methods using the modified silica gel and carbon column chromatography ⁴⁾. To the final extract 10 µl of external standard were added, which contained ¹³C₁₂-1,2,3,4-TCDD and ¹³C₁₂-1,2,3,7,8,9-HxCDD.

The analytical instrument system consists of a VG AutoSpec-Ultima high-resolution mass spectrometer and a Carlo Erba 8035 series gas chromatograph [MS: SIR, Resolution 10,000 at 10 %, EI+, 36 eV, PFK lock mass check, observation of 2 ions for native and labelled isomers, setting of 5 time windows; GC: columns: I&W Scientific, DB-5, 60 m, 0.25 µm; temperature program: 140°C (1 min), 15°C/min, 220°C (20 min), 4°C/min, 300°C (15 min); injector: 270 °C, splitless (2 min); injection volume: 1 µl].

Table 1. PCDD/PCDFs levels in the blood samples of Ufa phenoxy herbicide workers in comparing with some data published, calculated on lipid basis (pg/g).

	<u>Phenoxy Herbicide Workers</u>			<u>General Population</u>				
	w.1 sex-M,	w.2 age-	w.3 53-54	Mean UFA n=3 This paper	Mean Sweden n=5 Rappe 1994	UFA n=100 Schecter 1992	Russia n=68 Schecter 1992	Germany n=102 Schecter Päpke 1992
Dioxins								
2,3,7,8-TCDD	15,1	15,6	12,0	14,2	17	12	4,4	3,6
1,2,3,7,8- PnCDD	ND	5,5	ND	2,2	22	9,5	8,8	13,8
1,2,3,4,7,8- HxCDD	0,6	ND	ND	0,5	4,5			10,9
1,2,3,6,7,8- HxCDD	2,9	2,7	1,9	2,5	43	6	10,6	54,6
1,2,3,7,8,9- HxCDD	1,0	0,8	0,9	0,9	18	ND	2,3	10,6
1,2,3,4,6,7,8- HpCDD	5,1	2,6	5,3	4,3	87	9,7	13,5	92,4
OCDD	31,4	20,8	29,6	27,6	750	73	85,2	610,3
Dibenzofurans								
2,3,7,8-TCDF	2,1	6,5	0,9	3,2	0,34	ND	2,3	2,0
1,2,3,7,8- PnCDF	1,7	0,5	ND	0,9	34		ND	2,3
2,3,4,7,8- PnCDF	7,4	3,8	4,2	5,1	9,4	8	9,9	37,0
1,2,3,4,7,8- HxCDF	5,1	3,2	2,7	3,7				15,4
1,2,3,6,7,8- HxCDF	1,8	1,9	1,3	1,7	8,2	7	13	13,3
1,2,3,7,8,9- HxCDF	3,8	0,8	3,6	2,7	2,6			1,7
2,3,4,6,7,8- HxCDF	4,4	2,3	7,3	4,7	0,16	8,4	1,3	4,3
1,2,3,4,6,7,8- HpCDF	4,3	2,8	2,9	3,3	12		6,1	23,4
1,2,3,4,7,8,9- HpCDF	1,5	0,6	1,4	1,2	0,21			1,5
OCDF	16,2	7,5	8,0	10,6	2,5		8	4,2
Summed TEQ	21,1	22,2	15,9	20	56	23	17	42

The recovery rate is typically in the range of 55-104 %. The detection limits (S/N=3/1) are < 1 pg/g on lipid basis.

3. Results and Discussion

The Table 1 summarises the measurement results as well as some others authors data, which were attractive from the view-point of comparing with our results.

The high concentration of TCDD in the blood samples analyzed and the low one of all others PCDD and PCDF congeners are noteworthy, this leads to the TEQ values for the samples between 16 and 22 pg/g (lipid basis). These values correspond to the background levels for UFA, measured by A. Schecter -23 pg/g (n=100) and for some Russia cities -17-19 pg/g (n=68) ¹⁾. The TEQ values for the general population of USA amount to 41 (n=100), that of Germany-42 (n=85) ⁵⁾ two times as high as background levels in Russia at expense of considerable concentration of all others congeners with an exception of TCDD (3-5 pg/g).

The most similar exposure situation in Ufa is one discussed in the report of C.Rappe⁶⁾. The blood samples of 5 workers of chloro-phenoxy herbicides plant in Sweden have been analyzed, that produced in the late 1970s the 2,4,5-T, 2,4-D and 2,4,6-trichlorophenol (the capacity of this plant is 20 times less than that in Ufa).

The Table 2, Figure 1 and Figure 2 illustrate the ration of TCDD, total PCDDs (except TCDD), total PCDFs in blood samples of the workers from the similar plants in Ufa and in Southern Sweden.

Table 2. Blood concentration of PCDD/PCDFs in 2,3,5-phenoxy herbicide/chlorophenol production workers from Ufa (Russia) and Southern Sweden.

Congener	Blood concentration (pg/g extracted fat)	
	Ufa, n=3 mean	Sweden, n=5 mean
TCDD	14,2	17
Other PCDDs	36,8	924,5
Total PCDFs	37	69,4
TCDD, TEQ	14,2	17
Other PCDDs, TEQ	1,35	19,2
Total PCDFs, TEQ	4,2	19,8
Total PCDD/Fs, TEQ	20	56

4. References

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