

TIME HISTORY OF PCDD/Fs CONTENT IN BLOOD OF THE POPULATION IN THE CITY OF UFA, BASHKORTOSTAN

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Introduction

The city of Ufa in the Republic of Bashkortostan is a well-known place of dioxin pollution in Russia caused by industrial production of 2,4,5-T and 2,4,5-TCP during the 60s-80s. Extreme pollution of industrial zone (10-15 ppb), landfill sites of toxic industrial waste (200 ppb), suffered workers (100-1000 TEQ pg/g lipids) and higher levels in blood of the urban population were stated in a series of papers [1-5].

Thus in a pool sample of 100 donors selected in 1992 there were 27.5 pg/g lipids WHO/TEQ [4, 5], in 1995 the mean value for 3 donors in Ufa aged 23 ± 2 made 21.1 pg/g of blood lipids [6]. The content of 2,4,7,8-TCDD was rather high – 12-15 pg/g of lipids.

In 1997 samples were taken from 44 non-exposed donors aged from 5 to 70. For calculation of the background level of PCDD/Fs in blood for Ufa statistical data on the age of the population was used. Weighted average value of the background level in Ufa was 17.4 pg/g of lipids for 2,3,7,8-TCDD and 37.8 pg/g of lipids WHO/TEQ. The mean level was 45.4 WHO/TEQ pg/g of lipids. It was found that PCDD/Fs levels in blood considerably depend on the age [7].

Background levels of 2,3,7,8-TCDD by 2-3 times exceeding the known data for other industrial cities testify to the impact of the plant's polluted area situated within the city boundary [8]. Sharp distinctions in the levels of PCDD/Fs in blood depending on the age point to the history of man-caused pollution in the 60-80s, considerable concentrations have been determined just in the blood of people aged over 50.

For the recent five years rehabilitation of the Chimprom plant area has been carried out including dust-depressing and reduction of PCDD/Fs emission from incinerators. Most efficient was the reduction of emission volumes that has been registered for the last 4 years judging by fivefold reduction of snow cover pollution (a matrix accumulating emissions for nearly half of the year).

For assessment of dynamics of changes in blood of permanent residents in Ufa next stage of PCDD/Fs monitoring was carried out in 2000. An attempt was also made to evaluate "the urban effect" by studying the level of PCDD/Fs pollution of people living in Ufa only for 2 - 3 years.

Methods and Materials

Samples were obtained from 15 individuals. Occupational exposure was preliminarily excluded, diet peculiarities were not stated, all donors had been living in the city for the last 10-15 years. Five persons were not permanent residents of Ufa, previously they lived in Kazakhstan and Uzbekistan. This group was compared with a group of donors from Ufa of the same age bracket.

For analysis 40-50 ml of whole blood were sampled and frozen at minus 18°C. Labelled surrogate PCDD/Fs compounds were added to unfrozen blood. Analysis of whole blood samples was performed by denaturing with ethanol and ammonium sulphate.

Extraction was carried out by three portions of solvent mixtures of hexane/diethyl ether (2/1) and twice by hexane/diethyl ether (1/1). After gravimetric determination of lipids in evaporated extracts the lipids were decomposed and fat was removed. The extracts were purified by column chromatography with the use of SiO₂, Al₂O₃ and Carbopac-C/Celite 545. PCDD/Fs quantitative analysis was performed by HRGC/HRMS in compliance with 1613 US EPA methods with the use of non-polar capillary column DB-5 MS (60m) and a high-resolution mass spectrometer (Autospec-Ultima, 10000, UK). The degree of recovery made 43-106%.

Results and Discussion

So for the population of Ufa the following data were obtained:

1. In 1992 there were 2 pool samples by 30 people each that demonstrated PCDD/Fs presence at a level of 27.5 pg/g of lipids. The second sample – 130.6 pg/g of lipids - probably contained blood samples of exposed workers. There is no explanation of such a high level of PCDD/Fs content in paper [4] and we also leave this value without any comments.
2. In 1997 there were individual samples drawn from 44 residents within the age range of 6-70.
3. In 2000 there were individual samples drawn from 15 Ufa residents within the range of 20-75 years old and 5 samples from residents who had come from some regions of the former SU.

Table 1. PCDD/Fs in blood samples from the population of Ufa, Russia, pg/g lipids

PCDD/Fs	1992, n=30 [4]	1997, n=44 [5]		2000, n=15 [new data]	
	Pool	Mean	Median	Mean	Median
Age range	Unknown	6-76		20-80	
2378-TCDD	12.0	21.8	17.9	14.6	9.8
12378-PnCDD	9.5	13.6	12.7	11.9	9.9
123478-HxCDD	6.0	6.5	5.3	7.7	4.6
123678-HxCDD		10.7	8.5	12.6	12.8
123789-HxCDD	ND(3)	5.6	4.9	5.8	5.2
1234678-HpCDD	9.7	17.4	18.1	24.1	18
OCDD	73	92.3	86.9	76.5	81.9
2378-TCDF	ND(2)	6.5	5.3	23	16
12378-PnCDF	NA	10.1	7.2	9.5	8.2
23478-PnCDF	8	18.9	20.3	23	18.6
123478-HxCDF	7.0	13.8	12.6	16.2	12.2
123678-HxCDF		7.5	6.3	11.9	9.8
123789-HxCDF	NA	5.7	3.8	6.5	3.9
2346678-HxCDF	ND(3)	5.9	4.2	7.2	5.3
1234678-HpCDF	8.4	16.0	12.7	20.6	14.4
1234789-HpCDF	NA	7.3	5.6	5.5	4.3
OCDF	NA	26.2	17.9	62.9	42.9
TEQ-WHO, pg/g lipids	27.5	45.	41.2	37.8	28.5

ND = ½ MDL.

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HUMAN EXPOSURE II -POSTER

Table 2 PCDD/Fs in blood of Ufa residents and new-comers, pg/g lipids

PCDD/Fs	Mean, 1997		Mean, 2000	
	Residents	New-comers (from Uzbekistan)	Residents	New-comers (from Kazakhstan)
	22 ±2 age	21±3 age	38±2 age	40±1 age
2378-TCDD	5.9	2.5	7.9	0.8
12378-PnCDD	6.1	2.3	9.5	1.8
123478-HxCDD	2.3	5.9	1.3	3.0
123678-HxCDD	5.0	7.1	6.9	4.5
123789-HxCDD	2.7	4.7	2.0	0.8
1234678-HpCDD	10.4	25.0	12.2	17.6
OCDD	43.7	100.7	84.8	81.9
2378-TCDF	9.4	4.1	11.1	0.8
12378-PnCDF	6.4	8.1	4.5	6.4
23478-PnCDF	11.3	12.5	11.4	18.6
123478-HxCDF	10.1	4.4	7.5	15.1
123678-HxCDF	7.8	10.6	7.1	6.1
123789-HxCDF	3.7	7.5	1	3.9
2346678-HxCDF	5.1	16.3	4.3	0.5
1234678-HpCDF	9.7	35.3	7.3	14.4
1234789-HpCDF	2.6	4.3	1	2.5
OCDF	10.1	43.1	22.1	17.2
WHO/TEQ	22.8	18.2	27.6	16.0

As it is seen from table 2 PCDD/Fs spectres in blood of Ufa residents sufficiently differ from the ones of other regions. Data of tables 1 and 2 confirm increased 2,3,7,8-TCDD and 1,2,3,7,8-PnCDD content in samples of Ufa donors. This also gives indirect assessment of "the urban impact" on the new-comers living in Ufa less than 3 years by absence of changes in PCDD/Fs levels in blood what testifies to inconsiderable current emission and corresponds to our conclusions about dioxin intake together with foodstuff [9]. At the same time the impact on the population in the past is confirmed because levels in blood of people over 60 are considerably higher than the background levels in the region.

The background level in Ufa has somewhat lowered for the last 3-5 years. This is a favourable tendency marked in other papers though on national basis [10, 11].

Due to special conditions and history of PCDD/Fs pollution in Ufa it is more reasonable to use for monitoring of dynamics the data on PCDD/Fs content in blood normalised on the population of definite age groups. Demography figures for Ufa have changed for the last 5 years, these figures have been taken into consideration when making calculations of mean data for Ufa (natural growth of less exposed population aged 25-40).

These data are as follows (the data are given in paper [8] and converted into WHO/TEQ) :

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- In 1997 year - 37.8 pg/g lipids TEQ/WHO and 17.4 pg/g 2,3,7,8-TCDD;
- In 2000 year -31.8 pg/g lipids TEQ/WHO and 14.2 pg/g 2,3,7,8-TCDD.

In spite of some reduction of mean values for the population as a whole the analysis of dependence of TCDD content (or TEQ) on the age of donors within a wide range for the past years has shown that the differences between them are not statistically significant what generally testifies to a long period of semi-ejection:

- In 1997 year – $2,3,7,8\text{-TCDD} = 0.4\text{Age} + 1.6;$ $\text{TEQ/WHO} = 0.8\text{Age} + 4.5;$
- In 2000 year – $2,3,7,8\text{-TCDD} = 0.2\text{Age} + 7.4;$ $\text{TEQ/WHO} = 0.6\text{Age} + 15.4.$

Probably this approach will be useful for analysis of load on population in cities similar to Ufa that still experiences after-effects of pollution caused by industrial production of phenoxyherbicides or some accidents with possible time reference.

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