REZULTS OF BIOMONITORING IN A DIOXIN POLLUTION RISK ZONE IN UFA (1996-2014)

Amirova Z *

Environmental Research&Protection Center, 450075, 147, October Avenue, Ufa, Russia

Introduction

Existence of a pollution zone in the territory of the chemical plant ("Ufakhimprom") and the city of Ufa, Povolzhie, Russia, that for 50 years had been producing chlorphenol products including 2,4-D, TCP and butyl ether 2,4,5-T was rather in detail described in previous papers[1-4].

Chlorine and herbicide productions were closed in 2004 but conservation of the dioxin pollution zone was not performed. At present diphenylolpropan (Bisphenol-A) production and a medical waste incinerator are operating, destruction of polluted buildings is carried out. The process of liquidation of the "hot spot" pollution within the borders of the city with the population over 1 million people has not yet begun. The situation results in "spreading" of local high pollution zones over the territory including residential areas[5]. Many years of emission from incinerators of oil refineries and dust from the chemical plant resulted in increased dioxin level in biotissues of the population of Ufa.

Practically all former workers of the "Ufakhimprom" have the level of dioxin in blood by 5-10 times exceeding the background level of the city population[3]. At present among them there are cohort groups of exposed workers with dioxin content in blood of 250-400 pg TEQ/g lipid, but the groups of dioxin affection have not been admitted as those, people have no social protection. Remote effects of exposure were found[6]. For the population of Ufa in total an increased level in biotissues was also determined (blood, breast milk, fat, placenta)[7].

The phase of research related to PCDD/F content in blood of children born mostly after the closing of the Khimprom plant and living in districts of Ufa at different distances from the plant (1.5-20 km) was carried out. Under conditions of continuous emissions from the pollution hot spot it is especially important to carry out periodical measurements of dioxin content in biotissues of the population for revealing trends and for assessment of the results of activity/inactivity on rehabilitation of pollution zones.

Materials and methods

Whole blood and/or blood serum samples were taken from donors who had no professional contacts with chlororganic products, in compliance with ethic norms and according to voluntary agreement. No peculiarities or considerable differences in diet were found (mostly meat and dairy products, relatively low consumption of fish, inconsiderable consumption of fish from local rivers).

The content of PCDD/Fs was determined by the method of high resolution chromato-mass-spectrometry in compliance with the methods of US EPA 1613. Extraction methods were used for sample preparation. In all samples the content of lipid fraction was determined. The clean-up procedure was performed by classical methods: multi-layer SiO_2, Al_2O_3 and Carbopac-C/Celite columns. For separation of high-molecular compounds in the process of preparing human milk, blood and fat samples and other diagnostic human liquids the method of gel-chromatography was used. For PCDD/Fs measuring a high-resolution mass spectrometer (Autospec-Ultima, Waters, UK) and a series of isotope-labeled standards (CIL Corp.) were used in compliance with the US EPA 1613 method. Separation of PCDD/F isomers was carried out on a non-polar capillary column Restek RTX-Dioxin 60 m long. The results of PCDD/Fs determination are given in the scale (TEQ-WHO) with the use of toxicity equivalent factors (WHO/TEF_{2005}). The data received earlier were reduced to TEF_{2005} coefficients.

Results and discussion

At present the population of the city is exposed to emission of polluted dust particles from the pollution zone but 30-35 years ago the impact was much more considerable (chlororganic waste incinerators were functioning, accidents and fires took place on chlorine, chlorphenol production plants, 2,4,5-T and 2,4-D production was operating). Because of this the first research in 1992 showed high content of 2, 3, 7, 8-TCDD in blood of the population (12-15 pg/g blood lipid)[2]. It is known that dioxin content in human blood at the background level depends on the diet, individual peculiarities of metabolism, amount of fat, sex (breast feeding) etc. However the main factor is the time of accumulation, the age of the individual.

In 1997 samples from 44 non-exposed donors aged from 5 to 76 were taken. So for calculation of PCDD/F background level in blood of the Ufa city residents the statistical data were used on the number of people of different age. Weighted average made 17.4 pg/g lipid of 2,3,7,8-TCDD and 37.8 pg/g lipid WHO-TEQ. The mean value made 45.4 WHO-TEQ pg/g. For assessment of trends of PCDD/F accumulation/excretion in blood of permanent Ufa residents in 2000 individual blood samples from 15 permanent dwellers of Ufa were analyzed. The background level in Ufa for the period of 1997-2000 has practically not changed and made 35.9 pg/g lipid TEQ and 11.6 pg/g lipid 2,3,7,8-TCDD (weighted average value in relation to age). Studying of the effect of PCDD/F accumulation in Ufa was continued and in 2012 these levels amounted to 25.64 pg TEQ PCDD/Fs/g lipid and 4,14 pg/g lipids of serum.

It was found that the least data scattering of PCDD/F content is characteristic for the group of 20-30, with the increase of the age this factor also increases. Therefore age peculiarities of donors were selected as the main factor in assessing dioxin accumulation in blood, grouping in this case results in more precise values (table 1).

In 2012 analysis of pool samples of donors in Ufa was carried out showing that the mean level of dioxin content in blood , in the joint group aged 24-66 makes 25.64 pg/g lipid. In the group below 30 the level is about 10.0 pg TEQ PCDD/Fs/g lipid. As compared with the data of monitoring in 1977-2004 these values are somewhat lower, which means that the background PCDD/Fs level in blood of Ufa residents has a tendency to reduction more clearly expressed in the narrow interval of donors' age.

Table 1. Dioxin content in blood of donors in Ufa (aged 19-25)

Date (years)	1995	1996	1997	2000	2003	2012
Age	23±2	24±2	22 ±2	26±2	19±0	24±2
Number of donors	N=2	N=7	N=14	N=7	N=5	N=4
2,3,7,8-TCDD	6.13	6.47	5.9	5.9	4.8	5.76
1,2,3,7,8-PnCDD	11.65	11.06	6.1	8.4	5.45	1.21
1,2,3,4,7,8-HxCDD	2.12	3.3	2.3	1.9	1.05	2.54
1,2,3,6,7,8-HxCDD	2.78	6.92	5.0	7.12	1.15	2.07
1,2,3,7,8,9-HxCDD	3.56	3.17	2.7	2.7	1.25	2.69
1,2,3,4,6,7,8-HpCDD	11.12	16.56	10.4	9.13	1.35	17.69
OCDD	38.97	80.83	43.7	74.8	77.4	30.0
2,3,7,8-TCDF	2.01	2.98	9.4	8.23	17.0	1.0
1,2,3,7,8-PnCDF	3.56	3.35	6.4	6.5	4.0	1.38
2,3,4,7,8-PnCDF	18.36	16.39	11.3	16.4	23.3	1.31
1,2,3,4,7,8-HxCDF	5.12	9.25	10.1	5.5	2.3	2.76
1,2,3,6,7,8-HxCDF	5.14	6.35	7.8	7.1	4.5	2.92
1,2,3,7,8,9-HxCDF	1.01	2.72	3.7	ND	2.5	3.76
2,3,4,6,7,8-HxCDF	ND	4.82	5.1	4.3	2.2	3.54
1,2,3,4,6,7,8-HpCDF	2.17	7.37	9.7	7.3	8.18	4.23
1,2,3,4,7,8,9-HpCDF	4.85	3.23	2.6	1	1.0	4.0
OCDF	3.54	0.64	1.1	2.1	2.5	3.12
WHO-TEQ-2005	25.76	26.79	20.43	23.29	20.68	9,8

A special group of donors consisted of children of preschool and school age living nearby the pollution zone and in other districts of the city. If babies' intake via breast milk (increased daily doze) has been studied properly enough then for elder children data are more scant. At the same time dynamics of intake with food and removal of toxicants received in babyhood have some peculiarities due to increased metabolism, distribution of toxicants because of growth of biometric characteristics: the effect of dilution, tachytrophism[8].

In 2013-2014 sampling was carried out from 265 donors – children from 7 districts in Ufa located at a distance of 0.8 to 18 km from a potential emission source. In the district close to the industrial zone a group of elder children was selected (aged >16) and also the children of the parents connected with chemical production (table 2).

Table 1. Dioxin content in blood of children in Ufa

Groups of donors	Number of donors	Age	Distanse from Khimprom, km	TEQ PCDD/Fs, pg/g lipids		
				min	max	average
Area near the plant	47	8-12	1.0-2.0	11.83	17.83	14.83
Area near the plant	27	>16	2.5-3.5	3.58	10.75	7.15
Area near the plant	27	8-13	1.5-2.5	21.37	47.93	34.65
Area near the plant, parents-workers of chemical plants	17	7-12	1.5-3.5	6.65	26.71	17.33
Residential neighborhoods	18	6-10	4.25	ND	7.84	3.92
Preferential emission distribution area	22	8-13	17	3.8	19.86	9.9
Residential neighborhoods	30	7-12	8.3	2.13	9.55	4.78
Residential neighborhoods	22	6-10	16.5	ND	12.31	6.16
Residential neighborhoods	30	7-12	8.3	ND	6.3	3.15
Residential neighborhoods	35	9-12	8.3	ND	6.63	3.31

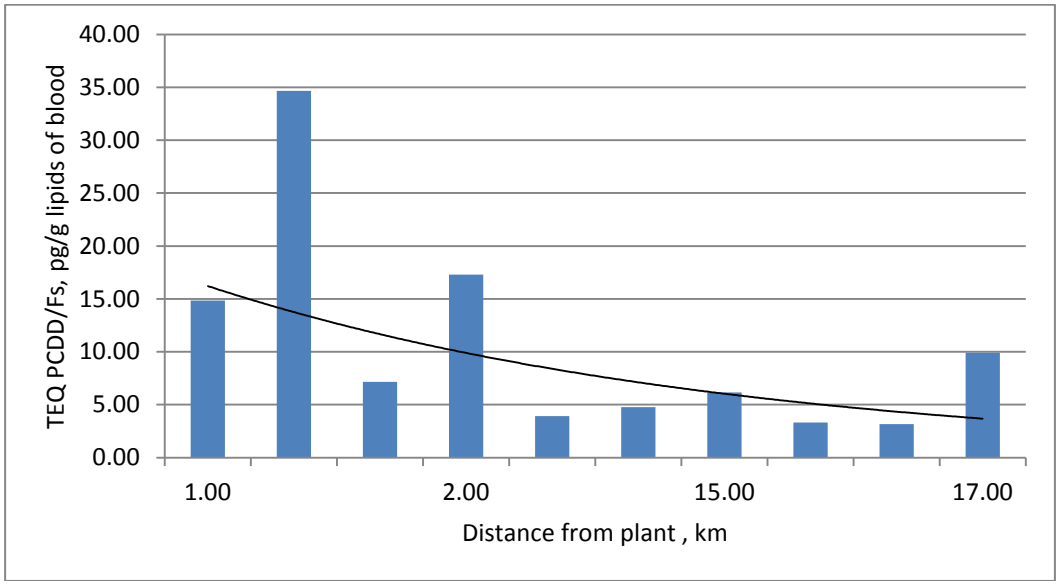

Figure 1. PCDD/Fs in blood of Ufa children

References

1. Weber R, Gaus C, Tysklind M, Johnston H. et al. (2008) Environ Sci Pollut Res. 15:363-93
2. Schecter A., Ryan J., Papke O. Chemosphere, 1994, 29, 9-11, 2361.
3. Amirova Z, Kruglov E. (2005) *Organohal Comp.* 67:2094-97
4. Amirova Z, Kruglov E, Maystrenko V, Khizbullin F. (2006) *Organohal Comp.* 68: 2225-28
5. Amirova Z, Khalilov R, Tagirova N (2012) http://www.dioxin20xx.org/pdfs/2012/1307.pdf
6. Ryan J, Amirova Z, Carrier G (2002) Environ Health Perspect 110:A699-701
7. Amirova Z, Kruglov E (2001) Organohal Comp 52: 269-273
8. Kerger B, Leung H, Scott P, Paustenbach D. Toxicol Sci. 2007;100:224–237.