IDENTIFICATION OF LOCAL POLLUTION SOURCES NEARBY THE MEGA-ZONE OF PCDD/F INDUSTRIAL POLLUTION, UFA, RUSSIA

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Abstract
Sources of high local pollution near a mega-zone of dioxin pollution - the plant Khimprom in the city of Ufa, Russia, South Ural - have been investigated. The sources of local PCDD/Fs pollution have been formed as a result of emissions from chlororganic waste incinerators, explosions, accidents and fires that had taken place at the plant for 50 years of its operation. All this and also existence of deserted toxic waste disposal sites of 2,4,5-T and 2,4,5-TCP production provide for many years of dioxin transfer by particles of polluted dust.
Dioxin pollution of the territory of the Herbicide Research Institute and of its testing ground is connected with laboratory synthesis and production of pilot amounts of 2,3,7,8-TCDD technical product.
It has been stated that the toxic waste disposal site still contains over 200 ppb TEQ PCDD/PCDFs. The territory of the herbicide testing ground of the Herbicide Research Institute are polluted up to 4 ppb TEQ PCDD/Fs.
In blood of women who had carried out laboratory synthesis of 2,3,7,8-TCDD from 400 to 1200 pg TEQ PCDD/Fs/g lipids have been found. The blood of those women' daughters born after exposure contains from 42,3 to 94 pg/g lipids of TEQ PCDD/Fs.

Introduction
The fact of existence of a polluted mega-zone in the territory of the chemical plant in Ufa is rather in detail described in our previous reports.[1-3]. The Khimprom for 50 years has manufactured chlorphenol products including 2,4,5-TCP and 2,4,5-T. Now the plant has been stopped but the process of elimination of the pollution source near the city with the population over 1 million people has not yet begun. The pollution level of accumulated soil and sludge is high. It is estimated on average as 15-20 ppb. Approximately up to the same levels production buildings are polluted. However for full assessment of the situation and planning of measures for rehabilitation it was necessary to have data on adhering areas and detection of other local polluted zones near the plant. Such is the area of an old illegal toxic waste disposal site of the 60s. The area of the deserted disposal site according to preliminary examination may be about 1 km^2 with maximum revealed pollution of slit over 200 ppb.[4]
Another examined zone is the area of the settlement with the population of about 2000 people. The settlement is exposed to emission of the chloroganic waste incinerator belonging to the plant (3-5 km); the incinerator has been operating over 50 years. In the territory of the settlement the ground and also food products of vegetable and animal origin produced here are polluted. The inhabitants have been subject to PCDD/Fs exposure both as a result of transfer of polluted particles and aerosols and via nutrition chain. Similar examination was carried out in the territory of the Herbicide Research Institute where for many years and up to present day herbicides of different classes have been developed. Here during the 60s the technology development and laboratory production of 2,3,7,8-TCDD was carried out. Four women got high levels of dioxin "doze" a part of which was passed to descendants.

Materials and Methods
In 2006 samples of soil and material of buildings in the area of the Herbicide Research Institute were taken. In the area of the settlement soil was sampled from private vegetable gardens and school territory. Biosamples are presented by cow milk and hen's eggs from individual farms and also by samples of breast milk of 5 donors permanently living in the settlement. Blood of 4 chemical researchers who synthesized 2,3,7,8-TCDD during the 60s and blood of their children (n=2) was sampled and analyzed in 1997/98. The average level was 688 pg TEQ-WHO PCDD/Fs/g lipids[5] for mothers and 68 pg TEQ-WHO PCDD/Fs /g lipids for children.
For estimation of a true size of the local pollution zone 15 samples of soil and bottom sediment formed as a result of ground water rise were taken.
Standard methods of sampling soil and biosamples were applied. Extraction methods were used for sample preparation. 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 milk, blood and egg samples the method of gel-chromatography was used. For PCDD/Fs measuring a high-resolution mass spectrometer (Autospec-Ultima, VG, UK) and a series of isotope-labeled standards (CIL Corp.) were used in compliance with the USEPA 1613 method.

Results and Discussion

Local pollution zone No. 1 – a settlement.

PCDD/Fs content in soil of the settlement is given in Table 1. The results of pollution via breathing are reflected in higher PCDD/Fs levels in samples of hen eggs, cow and human breast milk (by 2 times as much in comparison with Regulation (EC) No 199/2006). Breast milk samples of 5 donors were taken in compliance with WHO methods and analyzed individually. It must be noted that the background level of breast milk pollution in the region is 17.8 pg/g[6].

Table 1. **Results of polluting a settlement by Khimprom emissions, Ufa**

PCDD/PCDF	**Soil, pg/g of dry weight**		**Food products, pg/g lipids**		**Breast milk, pg/g lipids, # of donors (years of age)**				
	garden	school	eggs	milk	#1(21)	#2(25)	#3(24)	#4(23)	#5(21)
2378-TCDD	12.44	16.00	2.11	2.16	10.95	20.80	19.08	20.19	23.09
12378-PeCDD	10.73	16.56	1.70	1.73	10.72	19.14	13.62	17.60	25.70
123478-HxCDD	3.83	3.60	ND(0.1)	0.24	ND(0.1)	0.07	1.89	2.50	1.54
123678-HxCDD	3.86	5.47	0.53	2.76	4.27	4.53	2.48	5.04	10.07
123789-HxCDD	3.34	5.04	0.32	0.72	0.44	0.26	0.62	1.70	1.79
1234678-HpCDD	18.79	30.06	0.86	4.20	3.79	2.49	2.40	9.81	7.59
OCDD	66.98	146.2	1.73	22.66	11.50	16.59	9.14	15.34	16.04
2378-TCDF	5.56	5.94	1.43	0.81	2.32	1.48	1.63	1.88	1.84
12378-PeCDF	1.09	1.64	0.95	1.55	0.29	0.82	0.69	0.78	0.55
23478-PeCDF	3.33	3.74	0.94	5.40	4.94	6.66	5.90	3.66	4.76
123478-HxCDF	0.92	2.10	0.98	2.38	1.73	2.63	3.04	1.74	1.90
123678-HxCDF	3.96	5.52	0.71	1.70	2.03	2.53	1.92	0.69	3.60
123789-HxCDF	ND(0.1)	ND(0.1)	ND(0.1)	ND(0.1)	0.16	0.36	ND(0.1)	1.35	0.91
234678-HxCDF	0.66	1.31	0.62	0.72	1.36	1.20	0.51	0.90	1.49
1234678-HpCDF	3.28	ND	0.48	1.45	1.43	1.11	0.32	4.53	6.19
1234789-HpCDF	1.74	31.92	ND(0.1)	0.50	0.22	0.52	0.18	0.62	1.10
OCDF	6.76	17.96	ND(0.2)	1.57	ND(0,1)	0.52	0.14	1.68	2.94
TEQ-WHO	**27.35**	**38.05**	**4.80**	**7.68**	**25.45**	**44.66**	**36.94**	**36.94**	**53.66**

Local pollution zone No. 2 – the Herbicide Research Institute.

PCDD/Fs pollution of the Herbicide Research Institute area and especially of the former testing ground (hothouses – now ruined and removed beyond the institute territory) most probably took place as a result of experimental work and herbicide testing. Thus 2,4-D and other phenoxyherbicides had been produced in Ufa up to 2005. A fact of development of technique for 2,3,7,8-TCDD synthesis and production of pilot amounts under laboratory conditions is known. The result of it is pollution of the area and exposure of people in whose blood 30 years later high PCDD/Fs concentrations are registered. Considerable amount of dioxins was found also in blood of their children (Table 2). As it follows from Table 2, 98% of contribution into TEQ-WHO of chemists is made by 2,3,7,8-TCDD what confirms the source of exposure – contact with 2,3,7,8-TCDD product.

PCDD/Fs content in soil in the area of ruined hothouses reaches 4000 pg/g, the soil between buildings is polluted unevenly: from 50 up to 400 pg/g. The material of buildings contains from 60 to 150 pg/g and more. Dust from the automobile road contains up to 180 pg/g and pollution is constantly being transferred by vehicles and dust to residential areas of Ufa that are situated at a distance of less than 1 km away. At the same place a city food market is situated what results in pollution of food products.

Table 2. **PCDD content in soil, material of industrial buildings and human blood**

PCDD/PCDF	Soil, dust, pg/g		Material of buildings, pg/g		Whole blood of donors-chemists, pg TEQ-WHO PCDD/Fs /g lipids			
	hothouse	**road**	**plaster**	**isolation**	**#1**	**#2**	**#3**	**#4**
2378-TCDD	46.5	138.0	42.4	56.3	147.5	271.5	951.8	1202.7
12378-PeCDD	195.5	7.9	114.0	17.6	20.0	23.8	29.3	36.3
123478-HxCDD	77.9	0.4	0.1	ND(0.1)	6.9	11.4	8.0	7.0
123678-HxCDD	68.1	3.0	19.3	39.3	21.7	20.8	19.7	18.8
123789-HxCDD	50.0	3.0	9.9	10.3	16.2	14.3	8.0	11.9
1234678-HpCDD	32.5	35.2	73.1	410.2	22.8	30.4	21.3	23.0
OCDD	7162.6	570.4	229.1	2922.8	109.2	119.5	109.5	89.5
2378-TCDF	30208.2	31.4	382.3	29.2	3.4	6.6	6.0	14.5
12378-PeCDF	802.0	37.8	61.9	14.7	15.0	18.0	9.0	11.4
23478-PeCDF	467.6	23.6	59.1	35.1	22.0	16.9	22.7	25.3
123478-HxCDF	227.6	76.4	91.8	19.8	20.1	20.5	ND(2.0)	ND(4.0)
123678-HxCDF	337.5	26.5	83.9	36.1	9.0	4.8	ND(2.0)	ND(4.0)
123789-HxCDF	302.8	10.0	11.1	2.2	5.0	5.0	ND(2.0)	ND(4.0)
234678-HxCDF	165.6	5.5	34.7	4.8	7.7	6.8	ND(2.0)	ND(4.0)
1234678-HpCDF	98.5	24.6	142.4	60.3	14.2	19.1	19.0	21.1
1234789-HpCDF	521.8	17.2	29.6	1.0	3.0	15.5	4.3	6.3
OCDF	94.0	111.5	426.7	524.7	49.0	76.4	20.8	25.5
TEQ-WHO	**3667**	**176.0**	**151.8**	**110,9**	**178.8**	**302.8**	**968.2**	**1240**

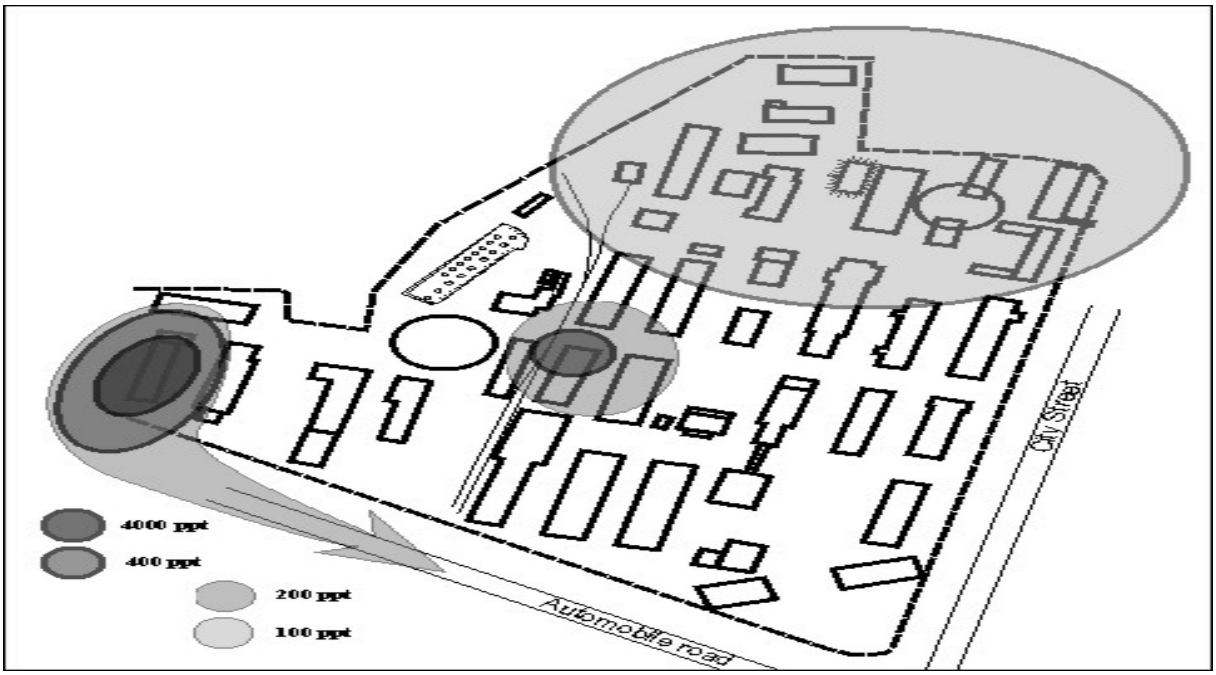

Figure 1. **The pollution map of zone No.2.**

Local pollution zone No. 3 – a deserted toxic waste disposal site.

A very complicated problem of planned Khimprom area rehabilitation is the task of conservation of this site. At present no work is carried out there and measures are developed on rehabilitation of the territory and burial of buildings.[3] Most important is rehabilitation of the deserted toxic waste disposal site of the 60s-70s. Burial of waste and even reaction mass was carried out without appropriate measures of environmental preservation what resulted in inevitable PCDD/Fs penetration to deep layers of soil and further transportation with ground waters. The situation is aggravated by the fact that the place of waste storage by its geological parameters is the lowest point in the plant area. So there occurs constant replenishment by ground and surface waters carrying PCDD/Fs polluted particles from the territory of the plant. The data given in Table 3 are preliminary. So far neither the depth of polluted layers nor precise contours of the local pollution zone are known.

Three zones of local pollution found near the plant of Khimprom in Ufa require measures for rehabilitation as well as the territory of the plant itself because one of them is a source of strong PCDD/Fs emission (No.3), the others two are hazardous for living (No.1) and for working of the institute personnel.

Table 3. **Pollution level of the deserted toxic waste disposal site near the Khimprom plant**

PCDD/PCDF	Soil, n=15, pg/g of dry weight		Bottom sediment, pg/g of dry weight	
	medium	Max	brook	ground waters
2378-TCDD	334.4	763.5	787.9	22952.7
12378-PeCDD	801.0	44000	98.0	11490.1
123478-HxCDD	288.4	26000	ND(1)	1313.9
123678-HxCDD	725.6	75000	96 4	5929.4
123789-HxCDD	431.1	54000	ND(1)	2894.4
1234678-HpCDD	1431.1	170000	221.7	13834.5
OCDD	2919.9	54160000	8001.6	202363.7
2378-TCDF	228.3	17000	179.7	1735.5
12378-PeCDF	43.5	5796.3	ND(1)	2165.1
23478-PeCDF	57.2	5776.5	105.7	4628.5
123478-HxCDF	133.7	9847.0	170.7	6093.1
123678-HxCDF	42.8	4967.3	130.4	3871.2
123789-HxCDF	26.2	2621.8	ND(1)	1477.2
234678-HxCDF	44.6	3268.4	119.3	2032.2
1234678-HpCDF	343.2	21000	634.9	46259.7
1234789-HpCDF	75.9	6443.4	119.1	ND(13)
OCDF	3372	24000	11969.4	ND(10)
TEQ-WHO	**1391**	**6345.9**	**1020.2**	**196250**

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