MONITORING OF HIGH POLLUTION ZONES FORMED DUE TO PRODUCTION OF 2,4,5-T, TCP AND 2,4-D IN THE CITY OF UFA, RUSSIA (1983, 1996-2012)

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Introduction

The situation with the existence of a mega-zone of pollution in the territory of a chemical plant (the Public Corporation Ufachimprom) in the city of Ufa, the Russian Federation (zone A), that for 50 years had been producing chlorophenol production including 2,4,5-trichlorophenol and 2,4,5-T, was rather in detail reflected in our previous reports[1-4] and in the survey[5]. In 1983 the content of dioxins in the commercial product TCF was determined for the first time and it made 0.65 mg/kg of 2,3,7,8-TCDD[6].

The plant was brought to a stop in 2004 but it is hardly possible to say that there is a regime of conservation of a dioxin pollution zone because in the territory the level of pollution of which is not yet studied enough there still operates the production of diphenylolpropane (Bisphenol A). Now and then there also operates an incinerator of medical waste with no control over its functioning.

A process of elimination of the hotbed of pollution within the borders of the city with the population over 1 million people has not yet begun. According to our assessment the pollution level of industrial buildings is 5-18 ppb, pollution of soil in the territory of the plant - 0.2-10 ppb, the content in sludge pits is 3-70 ppb [1]. In the territory of the plant (about 150 hectares) there were 187 buildings and constructions for industrial and social purposes, hundreds of kilometers of ground-based viaducts of technological pipelines, 18 kinds of underground technological communications and 3282 sewage wells, 389 tanks of different purpose and also a system of sludge pits including an emergency pond and air tanks for biological treatment of wastewater.

In 2007-2008 eight large industrial buildings where chlorophenol production had been produced were destroyed down to the foundation. Construction breakage was stored in the territory of the plant without any protection measures. The equipment of practically all shops was dismantled and removed for utilization with no control of dioxin content; the technology and the level of cleaning are unknown.

Near the plant there is a place of burial of industrial waste from 2,4,5-T production in the 60s with the dioxin content at some points up to 200 ppb (zone B). This area is mainly covered with soil and grass and spreading of pollution from it occurs generally with ground waters, rains and dust in spring and autumn periods[3].

In Ufa there was one more highly polluted zone revealed by our laboratory (zone C) – it is near the Research Institute of herbicides[7]. No work on rehabilitation of this zone within the city boundaries is carried out. The situation results in spreading of zones of high local pollution including residential blocks. Delay of rehabilitation measures demands monitoring of areas near pollution hotbeds. Spreading of polluted soil, dust particles during the period of shops destruction was traced by us using snow cover, thaw water during the period of active snow melting and also during the period of showers in summer.

Materials and methods

The method of environmental monitoring with the use of snow is being used by the Hydro meteorological service in Russia, methods of sampling are standard[8]. In snow cover the information on POPs coming with atmospheric precipitation for 5 months is being preserved, in the South Urals a stable snow cover is being settled from November to March. The thickness of snow cover is varied from 60 cm to 1.5 m depending on meteorological conditions of the year.

For assessment of spreading dioxins by air transfer to nearby areas snow was sampled in the vicinity of hotbeds of dioxin pollution, in sanitary protection zones of plants (to 1 km), in park zones of Ufa and in places located from 1.5 to 7 km away from the epicenters of pollution. Snow samples taken in the places situated 20-30 km away from the industrial areas served as control samples.

Under climatic conditions of the region (vehement melting of large volumes of snow for some days in spring) a great amount of thaw water is formed including the areas polluted with dioxins. The main volume of thaw water in the industrial zone is being transferred to the treatment facilities, but there is uncontrolled sewage that was used for study. Rainfalls also result in periodical washout of polluted soil from the plant territory, in two other

zones storm discharge is not organized and pollution directly enters the city environment. Sampling of thaw water and storm sewage was made in 2010-2012.
Samples of snow (about 4 kg), melt water and rainfall run-off were filtered, dioxin content was measured in the filtrate and in the filter cake. The results were summed up. 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. A series of isotope-labeled standards (CIL Corp.) were used in compliance with the USEPA 1613 method. Determination of PCDD/Fs was carried out with the use of a measuring system consisting of a chromatograph Carlo Erba 8035 and a high resolution mass-spectrometer Autospec-Ultima (VG/Waters) in the mode of electronic impact (36 ev) with the resolution > 10 000. The absolute detection limit of 2,3,7,8-TCDD made 10 fg. PCDD/Fs isomer separation was carried out on a non-polar capillary column Restek RTX-Dioxin 60 m long. The results of measurements were presented in the TEQ/WHO_{1997}.

Results and discussion

The results of snow cover monitoring for the period of 1996-2012 in the area of the PC Ufachimprom are given in Table 1 and they confirm continuous emission from the polluted territory.

Table 1. Zone A. PCDD/Fs content in snow samples (pg/l)/(pg/g of precipitate)

Direction/ Distance*	1996	1998	2000	2006	2008	2011	2012
N-E, 100 m	27.4/249.3			10.8/68.7	38.4/228.3	6,0/143	15.3/158.5
N-E, 800 m		6.3/23.7		127.4/473			
N-E, 1300 m	3.4/47.2	2.5/12.6					
E, 600-700 m				11.5/100		4.2/143.8	14.7/386.2
E, 1300 m				3.9/29	5.4/50	3.4/100.5	5.1/140.2
S, 1300 m	5.7/67.9		4.5/35		5.7/100	5.7/171.3	
S, 2500 m				2.4/28.5		2.9/20	3.5/57.6
S-W, 300 м	10.2/116,8	5.2/30.8		6.05/59.7			
S-W, 1000			5.0/20.3	4.2/15.7	8.3/157.7	4.2/210.4	7.8/252.3
S-E, 700 -900 m					3.35/48.2	4.6/42.8	1.74/47.5
S-E, 7500 m				8.6/65.8	7.1/154.5	2.2/74.3	1.2/32

*-distance from the center of the plant

Spreading of pollution with dust particles more often occurs in the North-South direction what corresponds to the wind rose in the point of observation. The main polluted buildings are located in the southwest part of the plant; earlier here the levels of soil and building material pollution up to 10-15 ppb were found; in the northeast part there are sludge pits and polluted soil around them (10-70 ppb).
Transport by the air in winter results in complicated redistribution of pollution from these two sources of dust particles emission. The level of particles pollution found in the north Zone A is about 200-400 pg/g, in the south part of Zone A – about 100-200 pg/g. In 2008 when the buildings were destroyed higher levels of dioxins in snow cover in all directions were registered but a more considerable change in the character of emission was observed in the zone of destruction – in the southwest. The aftereffects are traced also in case of a long distance transport over 7 km to the southeast. A jump of dioxin content in snow in the east direction is connected with the appearance of an additional emission source – the area where construction breakage (bricks, plaster, construction parts) was stored.
Snow cover in the polluted area of Zone B (the Research institute of herbicides) was examined during the period of 2008-2012. The level of snow pollution near the object is invariably high (Table 2).
The main hazard of this zone is its location within the city boundaries. Monitoring of snow cover close to a “hot point” (Zone B) revealed active inflow of polluted dust into the air at a distance of up to 100 m; when moving further away from the source the dioxin content in snow falls. In the southeast direction 287.8 pg TEQ PCDD/Fs of dust in snow was registered due to transfer of polluted particles by automobile transport.

Table 2. Zone B. TEQ PCDD/Fs in snow samples (pg/l/)/(pg/g of suspended particles)

Direction/	2008	2010	2011	2012

distance from the center of zone B				
W-20 m		30,4/654		
W- 30 m	11.04/171	31.9/523	64.3/839	
W-500 m	5.7/67.9		57/173.1	
SW-130 m			1.6/48	3.3/105.4
SW-300 m			4.8/145	3.0/139.5
SW-500 m		6.2/124.5		4.4/144.1
SE-900 m				6.64/287.8
S-24000 m	0.45/12.5	0.31/11.3	1.0/44.2	0.17/11.2

This very area showed the maximum pollution level of surface flow from the territory in the period of snow melting and during rainfalls (Tables 3 and 4). The isomer composition is characterizes by prevailing of 2,3,7,8-TCDD isomer what is connected also with preproduction of 2,4,5-T and 2,3,7,8-TCDD in the 70-80s (Table 5).
Uncontrolled storm sewage from the territories of Zones A and B is an unstable matrix containing from 10 to 1000 pg/l PCDD/Fs what means the transfer of particles polluted with dioxins up to 200-20000 pg/g. Many years of washout from the territory results in pollution of the soil cover near Zones A and B, pollution of ground water, and is a component part of the resulting level of pollution in addition to the air transfer.

Table 3. Dioxins in brooks when snow is melting near the borders of plants, pg TEQ/g particles

Pollution source/year of observation	2010	2011	2012
Washout from the territory of the PC "Ufachimprom"	234.9-244.7	178.1-1830.1	338.5-1725.9
Washout from the territory of the Research Institute of herbicides	279.9-20115.3	154.0-8729.1	388.0-603.2

Table 4. Dioxins in brooks after a strong storm, pg TEQ/ g particles

Pollution source/year of observation	2011	
	pg/l	pg/g
Storm sewage from the territory of the PC "Ufachimprom"	7.7	127.5
Washout from the territory of the Research Institute of herbicides	1192.0	968.8

Isomer composition of PCDD/Fs in snow and products of its melting in Zone A (the chemical plant) considerably differs from pollutions found in Zone B (the Research institute) near old hothouses – the polygons for testing pilot batches of herbicides (Table 5).
If in snow samples from the plant territory furan compounds prevail – the products of burning processes, then the brooks washing out mainly soil particles have a reverse correlation of dioxins and furans and contain 2,3,7,8-TCDD in the concentration by several times exceeding its level in snow.
In Zone B there is another picture of isomer distribution – over 98% of the sample toxicity is due to the presence of only one isomer – 2,3,7,8-TCDD what testifies to some other source of dioxin pollution as compared with the consequences of pollution in the industrial zone of phenoxy herbicide production.
In spite of instability of snow samples composition depending on meteorological conditions, a complicated character of precipitation from the air adding to the main emission some traces of dioxin pollution from automobile transport, emergency flares and emissions from incinerators of oil refining plants situated near the area of investigation, the semiquantitative data of monitoring allow to assess the tendencies of changes in emission load from the "hot spot" of dioxin pollution.
Sampling of storm/melt water from polluted areas is not regulated and may be used as a confirmation of hazard of the revealed local zones of dioxin pollution.

Table 5. PCDD/Fs in samples of snow and melt water from the territories of Zones A and B

PCDD/Fs	Snow, Zone A	Brooks, Zone A	Snow, Zone B	Brooks, Zone B

	pg/l	pg/g	pg/l	pg/g	pg/l	pg/g	pg/l	pg/g
2,3,7,8-TCDF	316.86	85.34	38.70	113.83	4.12	53.78	19.36	12983
2,3,7,8-TCDD	40.04	10.78	180.61	531.20	61.92	807.61	2386.52	19887.67
1,2,3,7,8-PnCDF	576.75	155.34	57.82	170.06	1.68	21.87	8.98	74.83
2,3,4,7,8-PnCDF	283.09	76.25	38.81	114.15	2.04	26.61	5.66	47.17
1,2,3,7,8-PnCDD	41.93	11.29	241.19	709.38	0.03	0.39	19.36	161.33
1,2,3,4,7,8-HxCDF	576.75	269.25	97.86	287.82	2.00	26.04	12.92	107.67
1,2,3,6,7,8- HxCDF	283.09	100.12	44.60	131.18	3.44	44.83	6.02	50.17
2,3,4,6,7,8- HxCDF	999.68	43.36	33.57	98.74	1.63	21.26	1.42	11.83
1,2,3,7,8,9- HxCDF	371.73	23.55	5.08	14.93	0.03	0.39	3.36	28.0
1,2,3,4,7,8- HxCDD	22.29	6.00	136.86	402.53	0.03	0.33	1.2	10.0
1,2,3,6,7,8- HxCDD	99.27	26.74	542.08	1594.34	0.03	0.34	3.64	30.33
1,2,3,7,8,9- HxCDD	21.68	5.84	304.58	895.81	0.38	4.96	0.1	0.83
1,2,3,4,6,7,8-HpCDF	533.99	143.82	501.17	1474.03	6.10	79.61	12.72	106.0
1,2,3,4,7,8,9-HpCDF	279.46	75.27	49.39	145.26	0.06	0.76	0.12	1.0
1,2,3,4,6,7,8-HpCDD	441.81	118.99	1588.40	4671.76	3.69	48.17	10.88	90.67
OCDF	1217.02	327.78	4754.11	13982.69	4.71	61.48	94.16	784.67
OCDD	1152.39	310.38	5382.65	15831.32	32.16	419.43	160.94	690.5
TEQ PCDD	100.83	27.16	536.57	1578.15	62.03	809.09	2406.49	20005.41
TEQ PCDF	372.3	100.28	50.26	147.82	2.29	29.84	7.35	61.12
Total	473.14	127.43	586.83	1725.97	64.32	838.93	2413.84	20115.32

Acknowledgement
The research was carried out within the frame of the state assignment of the Ministry of Nature Management and Ecology of the Republic of Bashkortostan.

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