PCDD/Fs Contamination from Defoliants and Chlorinated Pesticides Production: Steps for Remediation of Stockpiles, Soil and Utilization of Contaminated Buildings

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Introduction

Beginning from the 40s in the former USSR a net of plants was created for production of chlororganic substances with the total production volume reaching 3 million tons in the 80s in the cities of Ufa, Chapayevsk, Rubezhnoye, Perm, Dzerzhinsk, Novocheboksarsk, Volgograd, Usolye-Sibirskoye, Novomoskovsk, Zima, Slavgorod, Saki and others.

The plant Khimprom in Ufa was oriented to production of chlorine, chlorophenol products and phenoxyherbicides. For 55 years of the plant operation several chlororganic products have been produced at large scale, among them most hazardous production of butyl ester of 2,4,5-T and 2,4,5-TCP (Table 1).

Samples of technical 2, 4, 5-TCP contained up to 0.65 mg/kg of 2, 3, 7, 8-TCDD[1]. 2,4,5-T production cycle included alkali hydrolysis of 1,2,4,5-tetrachlorbenzol and condensation with metachloracetic acid in butanol. In the process of production some stages were modified. Thus to speed up alkali hydrolysis and to increase the output of the final product the saponification was carried out at 300^0C and raised pressure what should inevitably result in PCDD/Fs formation.

Table 1. **Main products of Khimprom in Ufa from the beginning of functioning up to its shut down in 2004**

The start of production	Produced up to	Production volumes, t/year	Product
1954	1987	22700	Chlorbenzene
1959	2004	16600	Trichloroethylene, perchloroethylene
1962 1974	1974 1987	100-120 (35) 1000 (700)	2,4,5-TCP, (TCP-Cu) 2,4,5-TCP (TCP-Cu)
1964 1966 1966 1966	1967 2004 2004 2004	600-650 15500 20160 5780	2,4,5-T Butyl ester Monochloroacetic acid Chlorosulphonic acid Chloroamine
1966	2004	37300	Cl_2
1969	2004	14350	2,4-D Dimethylamine salt
1972	2004	10750	Epoxide resin
1973	2004	13000	Chlorinated methanes
1979	2004	2960	Lenacil (Venzar)
1981	2004		Malathion (Carbofos)
1988	2004		Phenol, 4,4'-(1-methylethylidene) bis
1960	2004	12800	Industrial waste burning
1988	Now	75000	Diphenylolpropane

At present the plant in Ufa is in the state of long-term conservation until a decision is made on the ways of decontamination and rehabilitation of the territory. Withdrawal of technological objects is carried on gradually from August to November, 2004. Now only diphenylolpropane production is functioning.

In the territory of the plant (about 150 hectares) there are 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. Eighteen production buildings were designed for manufacturing herbicides and polychlorobenzenes (o- and p-

dichlorobenzenes, tetrachlorobenzenes); in 4 more buildings hexachlorobutadiene, insecticides, heptachlorine were produced and new pre-production variants of herbicides were developed.
In the territory of the plant there are 495 tons of liquid chlorine still stored. In case of tanks depressurization contamination zone may be about 3.5 km, over 8000 residents of the nearby living blocks may suffer.
Over 600 thousand tons of activated sludge and lime sludge polluted with dioxins have been accumulated at the plant. For xxx years an incinerator for burning still bottoms has been functioning. Waste and sludge during many years were stored in the territory of the plant in 6 sludge pits, 5 of them are filled up. There are two stand-by ponds (Table 2). The total volume of accumulated waste is about 573.8 thousand tons including: lime sludge – 511.5 thousand tons, excess sludge – 62.3 thousand tons. Sludge pits Nos. 4-6 have been examined. The state of objects Nos.1-3 has not yet been studied. However considering the time of their usage there may be found maximum concentration of dioxins coming with TCP production waste.
Production of 2.4.5-T 2.4.5-TCP and herbicides 2.4-D was started in Ufa in 1962-1967, before construction of sludge pits. At that time production waste was stored right in the territory of the plant and beyond it in a nearby ravine. A case is known when about 8 tons of reaction mixture was washed out into the sewerage. Now there is an unauthorized landfill site the area of which is unknown. The site is fed by underground and surface water from the territory of Khimprom. Pollution level reaches 200 ppb[6]. The polluted zone is covered by soil and vegetation with strips of “dead” surface and it is a source of dioxin pollution by way of dust transfer and via automobile transport because it is situated near a road.

Objects and Methods
Most dangerous buildings and storages were examined for PCDD/Fs content [2-5]. PCDD/Fs determination was performed in compliance with the EPA 8280 methods. The measuring systems HRGC/LRMS: TRIO-1000 (1500), Carlo Erba 8035, DB-5 MS, 60 m, the detection limit was 0.3 ppb[2-4], and INCOS 50 (Finnigan MAT), Varian 3400, DB-5 MS, 30m, MDL-0.5 ppb [5]. 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 (Table 2,3).

Table 2. **PCDD/PCDFs content in samples of soil, wall plaster scrape and sludge of Khimprom, ppb**

PCDD/Fs	Soil		Wall plaster scrapes		Sludge pits, depth of sampling, cm		
	Shop TCP	Incinerator	Shop TCP	Shop 2,4,5-T	#4, >150	#5, 0-5	#6, 0-29
2378-TCDD	6.11	4.49	6.0	1.0	56.39	21.9	2.71
12378-PeCDD	0.93	5.97	0.84	0.18	<п.о.	7.28	13.95
123478-HxCDD	0.15	2.74	0.12	ND (1)	<п.о.	<п.о.	0.29
123678-HxCDD	0.60	7.08	0.48	0.18	<п.о.	<п.о.	5.94
123789-HxCDD	0.22	4.15	0.18	0.13	<п.о.	<п.о.	2.56
1234678-HpCDD	0.67	22.14	0.52	0.68	<п.о.	<п.о.	8.38
OCDD	4.32	42.31	4.83	10.0	2258.3	294.8	40.82
2378-TCDF	0.23	0.44	0.21	ND (5)	100.4	175.46	ND (2.5)
12378-PeCDF	0.07	0.86	0.06	0.12	<п.о.	3.59	0.33
23478-PeCDF	0.08	1.60	0.07	0.16	<п.о.	4.62	0.34
123478-HxCDF	0.16	1.65	0.13	2.21	<п.о.	4.94	0.83
123678-HxCDF	0.05	ND (2)	37.4	0.18	<п.о.	3.85	0.84
123789-HxCDF	0.03	ND (2)	0.03	0.15	<п.о.	4.78	0.11
234678-HxCDF	0.05	ND (2)	0.05	0.11	<п.о.	4.37	0.78
1234678-HpCDF	0.76	5.47	0.55	1.54	23.9	18.4	3.87
1234789-HpCDF	0.05	1.17	0.04	1.15	32.6	23.7	0.19
OCDF	5.61	30.58	4.39	23.0	1645.8	536.1	16.19
TEQ, PCDD/Fs	**6.76**	**10.04**	**6.60**	**1.54**	**70.9**	**45.3**	**11.18**

Such a long period of producing dioxin hazardous products resulted in pollution of the Khimprom plant territory. Soil samples from the plant territory contain dioxin from 0.4 to 10 ppb including the soil at the depth of several meters. The highest pollution was found in the samples taken near a chlororganic waste incinerator that had been a source of dioxin emission for a long time. Pollution of the area within the radius of 200 meters beyond the plant territory exceeds 0.2 ppb.

Results and Discussion

According to Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases[7] with the use of available data on the volumes of production of main chlororganic products the estimation of the total volume of PCDD/Fs formed during the plant operation was made. It is 2.5 kg TEQ PCDD/Fs, including: a) hazardous waste incineration (category 1b2)- 197 g (release to the air), 507 g (release in residues), b) 2,4,5-T (7b) - 0.06 g (release to the land), 16.8 g ((release to product), c) 2,4-D (7b4) – 351.6 g (product), d) TCP (7b2) – 16.7 g (product), i) chlorbenzene (7b1)– 29 g (product), f) chlorine (7b) – 1417 g (residues).

At present the data on dioxin pollution of soil, buildings and sludge is insufficient to make technical decisions on liquidation and conservation of the plant.

For assessment of the situation and making decisions on methods of polluted material elimination an additional research is planned. The volumes of work are to be estimated for decontamination, for assessment of pollution of roof, building material, sewage slit and residues in pipelines with other chlororganic compounds. Assessment of geological and hydrological peculiarities of the area is planned in order to construct burial grounds. Several variants of elimination or conservation are being considered:

1. Destruction of buildings, dismantling of equipment and burial of the remains in the territory of the plant with construction of long-term burial grounds using unfilled sludge pits and building new ones.
2. Using building constructions with inconsiderable pollution for construction works (road metal, crushed stone) in production areas of refineries in Ufa.
3. Covering of polluted material with soil and isolating materials.

Variants of decontamination of polluted materials and the experience of their use are also being considered[8]. Alongside with getting the lacking data on dioxin levels a most complicated is the task if interpreting a set of data on pollution and working out criteria for relating of soil, building constructions and sludge to one of the categories of pollution. Prohibitive amount in soil (without grading of soil use) set as far back as in 1986, in the former USSR, is 0.33 ppt. It is evident that the use of this value as a threshold value is impossible because the limited volume of data points to the current background pollution of soil in cities of Russia – up to 3-4 ppt[9].

Obviously we'll have to be guided by norms and criteria of other countries. Thus Residential Soil Remediation Criterion in the USA and Canada makes 1 ppb. German Guidelines for PCDD/Fs in dry soil permit pollution levels in industrial zones 1-10 ppb, in residential areas - 0.1-1.0 ppb. When reclaiming territories in Italy and Taiwan the same criterion, 1 ppb was applied[10].

When the plant was shut down its territory and the territory of unauthorized landfill sites became a real "hot spot" and its impact on the residential zone is continued due to dust particles transfer[4].

References

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ble 3. **Characteristics of sludge pits containing dioxins in the territory of the plant Khimprom, Ufa, Russia**

Sludge pits number	Working time	Area (ha), volume (m^3)	Humidity, %	Real vilume, m^3	Composition	State of sludge pit	Characteristics of sludge pit	TEQ PCDD/Fs, ppb
# 1	1968-1975	S=1.76; V=58,000	30%	V=58,000	Lime sludge	Out of work, covered with a layer of soil, vegetation	Protected by a dam of clay, reclaimed	NA
# 2	1968-1975	S=1.5; V=47,000	30%	V=47,000	Lime sludge	Out of work, covered with a layer of soil, vegetation	Protected by a dam of clay, reclaimed	NA
# 3	1968-1975	S=1.5; V=63,000	50%	V=61,250	Lime sludge	Out of work, free capacity: 1.75 thousand m^3	Protected by a dam of clay	11 ppb (2378-TCDD)
# 4	1968-1975	S=1.8; V=70,000	40%	V=70,000	Lime sludge	Out of work, filled up	Protected by a dam of clay	0-5 cm:3.9ppb 50 cm:17.3ppb 150 m:70.9ppb
# 5	1978-1985	S=1.1; V=42,500	40%	V=42,500	Lime sludge	Out of work, covered with a soil (1.5 cm)	Protected by a dam of clay	0-5 см:45,3ppb 50 cm:33.8ppb 150cm:51.9ppb
# 6	1988-2004	S=1.7; V=65,000	80%	V=56,060	Lime sludge, excess sludge	Surface is not covered. Free capacity: 8,940 m^3	Protected by a reinforced concrete wall, the bottom covered with asphalt concrete, crushed stone	0-25 см:15,3 ppb
# 7	1996-2003	S=1.5; V=29,300	40%	V=29,300	Lime sludge, excess sludge	Surface is not covered	Protected by a reinforced concrete wall, the bottom screened with concrete	>18 ppb
# 8	1992-2004	S=1.2; V=59,500	60-80%	V=53,170	Lime sludge, excess sludge	Surface is not covered. Free capacity: 6,330 m^3	Protected by a reinforced concrete wall, the bottom screened with concrete	NA
Depot of silt	1986-2004	S=0.7; V=5,000	40%	V=5,000	Excess sludge	Surface is not covered	Protected by a dam of clay	0-5 cm:3.8 ppb