ESTIMATION OF ENVIRONMENTAL CONTAMINATION LEVELS AND RELEASES OF PCDD/F FROM SELECTED FACILITIES IN THE TERRITORY OF RUSSIA

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Introduction

In order to establish objectively the actual scale and degree of contamination with dioxins and dioxin-resembling toxicants in the territory of the Russian Federation it is essential not only to identify contamination sources associated with dioxin-hazardous technologies, but also to assess strength of such sources from the standpoint of their environmental releases. As was demonstrated earlier in our works, in the territory of Russia the priority sources of environmental contamination with PCDD and PCDF are facilities of chemical industry producing chlorine-containing products, specifically those located in the cities of Chapaevsk, Ufa and Dzerzhinsk.[1] Two approaches can be pursued in assessment of dioxin releases from these plants: the first is instrumentation measurement of dioxin content in releases of specific sources and the second is estimation of possible releases of dioxins. For assessing releases and scale of environmental contamination with dioxins the methods were used based on the models proposed by scientists of SPA «Typhoon» .

Methods and materials

For estimation of the PCDD/PCDF releases from facilities of chemical industry we used the methodology of selective investigation which was developed in SPA «Typhoon» and includes sampling and analysis of key snow and soil samples from the area affected by activities of a given facility (not more than 25 samples).

The study focused the chemical facilities which produced dioxin-containing products up to the end of the 80s, namely the «Chimprom» in Ufa (production of herbicides based on 2,4-D; trichlorophenol and copper tricholophenolate, orthochlorophenol), the Srednevolzhsky plant of chemicals in Chapaevsk (production of lindane, pentachlorophenol, trichlorophenol); the «Azot» and «Orgsintez» plants in Novomoskovsk , Tula region (production of chlorine, « sovols») and the «Agrohim» plant in the town of Shchelkovo, Moscow region (production of trichlorometafos-3, 2,4,5-trichlorophenol, trichlorol).

During 1993-1999 the staff of the SPA «Typhoon» conducted studies of environmental contamination in the above mentioned cities. Samples of soil and snow were collected in the vicinity of assumed sources to be analyzed for PCDD and PCDF. The samples were analyzed in SPA «Typhoon» by the methodology similar to the EPA 8280 and the Russian methodology using GC/MS with chemical ionization and detection of negative ions (GC-MS CI NI)[2].

For calculation of atmospheric releases the model developed in the Institute of Experimental Meteorology/SPA «Typhoon» was used which accounts for characteristics of sources and pollutant properties, conditions of transport and dispersion in the atmosphere over long time intervals and wash-out by precipitation and deposition on the ground[3,4].

Results and Discussion

The magnitudes of dioxin emissions to the atmosphere from production activities and concentrations in the air, both at the time of investigation and retrospectively, were estimated based on results of measuring dioxins in snow and soil (in the international toxin equivalent M-TE). The results of modeling and actual measurements were compared using the technique of sequential approximations. In the paper more attention is given to results of the integrated survey of the city of Chapaevsk[5].

The flow of dioxins to the atmospheric air from chemical facilities in winter was estimated by measurements of dioxins content in snow. Based on the concentrations of PCDD and PCDF in snowmelt water referred to the unit area from which snow was sampled, the depositions of PCDD and PCDF were calculated (ng M-TE/m^2). Table 1 shows ranges of PCDD/F depositions estimated by measured concentrations in snow at a distance of up to 15 km from the facility and equal to 0.02-12.75 ng M-TE/m^2.

Table 1. Content of polychlorinated dibenzo-n-dioxins and dibenzofurans in snow samples (ng/m^2) in Chapaevsk

Compound	Snow depositions, ng/m^2 n=25		
	Min	Max	Average
2,3,7,8-TCDD	ND	0.71	0.10
1,2,3,7,8-PeCDD	ND	24.75	3.85
1,2,3,4,7,8-HxCDD	ND	6.87	1.20
1,2,3,6,7,8-HxCDD	ND	3.18	0.63
1,2,3,7,8,9-HxCDD	ND	5.42	0.55
1,2,3,4,6,7,8-HpCDD	ND	53.93	13.11
OCDD	1.32	255.85	46.05
2,3,7,8-TCDF	ND	ND	ND
1,2,3,7,8-PeCDF	ND	23.87	1.0
2,3,4,7,8-PeCDF	ND	4.94	0.2
1,2,3,7,8,9-HxCDF	ND	0.58	0.02
1,2,3,4,7,8-HxCDF	ND	16.19	2.17
1,2,3,6,7,8-HxCDF	ND	16.75	1.67
2,3,4,6,7,8-HxCDF	ND	ND	ND
1,2,3,4,6,7,8-HpCDF	0.20	55.56	8.04
1,2,3,4,7,8,9-HpCDF	ND	ND	ND
OCDF	0.34	43.69	9.05
(M-TE)	0.02	12.75	3.06

Note: ND- below detection limit (0.01 ng/m^2)

A preliminary analysis of the plant activities led us to conclude that releases to the atmosphere from the Chapaevsk plant in 1991-1994 were occasional. In different time periods the estimated emissions of PCDD/F were varying from 0.5 μg/s (15 g/year occurring frequently and considered to be routine) to 5 μg/s (150 g/year), which were infrequent and considered to be abnormal).

Estimates of concentration fields in snow cover over the entire study area for the routine release (15 g/year) and recalculated for the sampling time in 1994 are consistent with the measurements.
The retrospective estimates of the releases using soil data suggest that the release of dioxins over the whole period of plant operation is most likely to be within 20 kg. Based on this estimate, the field of PCDD/F content in soil and mean annual concentrations of dioxins in the atmosphere air for the time period of most intense activities were calculated. The mean annual concentrations in the air were exceeding even the mean daily permissible levels of dioxins (0.5 pg/m^3) not only within the city itself, but also in adjacent areas.
The comparative analysis of estimates of dioxins releases and concentrations in soil, depositions and air in the vicinity of the contamination sources in Ufa, Novomoskovsk and Shchelskovo is indicative of closeness of dioxin loading in Ufa and Chapaevsk (Table 2). The mean emissions for Ufa and Chapaevsk were found to be 900 t/year and 740 g/year in M-TE, respectively (25 kg and 20 kg M-TE for the whole time period over which the sources were active). The total annual release from the sources in Novomoskovks was 22.8 g M-TE and 0.9 kg M-TE over the whole period of the source action. The releases of PCDD/F from the Shchelkovo plant are characterized by about the same order of magnitude.

Table 2. Estimated releases and concentrations of dioxins (in M-TE) in soil, depositions and air in Ufa, Chapaevsk, Novomoskovsk and Shchelkovo (at a distance of 1.5-2.0 km from sources)

City	Release		Dioxin content, M-TE		
	Total, kg	g /year	Soil ng/kg	Depositions μg /m^2 Year	Air pg/m^3
Ufa	25	900	110 – 350	1.1 - 1.3	1.2 – 4.1
Chapaevsk	20	740	140 - 210	1.3 - 2.0	1.6 - 2.1
Novomoskovsk	0.9	22.8	20 - 30	0.03 - 0.05	0.16 - 0.07
Shchelkovo	0.3	15.0	4 - 8	0.01 – 0.03	0.1 – 0.2

With respect to the facilities in Chapaevsk and Ufa, it is known that the technologies used there for production of chlorophenols and their products were deficient for a long time and considerable environmental releases of dioxins were quite possible[6].
The derived estimates of dioxins from the sources located in Novomoskovsk and Shchelkovo are comparable to those included in international inventories of releases from similar facilities. Specifically, this applies to production of halogen-organic substances amounting to 0.1-0.3 g M-TE/year and incineration of chemical waste (the furnace for waste burning at «Azot» plant) which is close to 7.65 g M-TE/year in 1985 in Belgium[7]. As can be seen from Table 2, all environmental contamination indicators (the content in soil, air and depositions) in the cities of Ufa and Chapaevsk are one or two orders of magnitude higher those in Novomoskovsk and Shchelkovo.

Conclusion

Considering that there is no continuous monitoring of environmental contamination with PCDD and PDDF in the territory of Russia, the number of measurements of these chemicals in the environment is rather limited and measurements in emissions from the facilities are practically non-existent, the proposed calculation method can be used for preliminary estimation and prediction of dioxin loading from individual sources.

References

1. Pervunina R.I., Samsonov D.P., Rakhmanova T.I. (1992) Dioxin-92, Extended abstracts, 9, 173.
2. Samsonov D.P., and V.P. Kiryukhin. (1994) J Anal.Chem (Rus), 49 (8), 95-101
3. Senilov N.B., (1996) Industrial Air-Soil Pollution Model. Russia software patents 960082-960083
4. Malakhov S.G. and N.B.Senilov. (1993) Soil Science, 25 (2), 111-115
5. Sotskov Yu.P., Onishchenko T.L., Pervunina R.I. (1995), Report on R&D «Integrated studies of environmental contamination with dioxins in Chapaevsk», ATs GIN RAN SPA, «Typhoon», M.
6. Fedorov L. A. (1991) Chemistry and life, No 2, pp 30-35
7. De Fre and M.Weers (1995) Opgemaakt in Opdracht van de Vlaamse Milieumaatschappij (Ordermummer:941055). Stofdossier Dioxines-Eindrapport. MIE-DI-9459. January 1995.