Dioxins in Russia. II. The Republic of Komi.

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Introduction

The Republic of Komi (with the city of Syktyvkar as the capital) is situated in the North - East of the European part of Russia. There is wood industry, sawmill industry, woodworking industry and materials of construction industry. Near Syktyvkar there is a large woodworking complex (SWC).

As far as there are industrial productions forming PCDD/Fs, in 1997 an examination of the most hazardous area (Ezhva, Syktyvkar) was carried out by the decision of the Komi Government. Previously this region of Russia had never been examined for PCDD/Fs contamination.

Sampling was made by local bodies of Sanitary and Epidemiological Control, analytical measurements were made at the Environmental Research and Protection Centre (Ufa, Bashkortostan). For comparison blood samples from distant areas without technogenic impact were used (control group).

Objects and Methods

In the control area and in the area under examination pool samples of whole blood and breast milk were taken from permanent inhabitants. In the more hazardous area river water, waste water, soil, bottom sediments were sampled. Samples of freshwater fish caught in the river section where waste water of SWC are mixed with the river water were also taken.

The content of all 17 toxic PCDD/Fs isomers in samples of environmental objects and biological samples was determined by the methods of EPA 1613A, all procedures of quality control of the analysis were observed (1). Parallel experiments and idle control samples on model matrixes were carried out for all samples.

Sample preparation included extraction by individual solvents and their mixtures and subsequent purification by the method of liquid chromatography on the columns filled with Al_2O_3, on a multilayer silica gel column and graphitized black carbon (Carbopack/Celite), described earlier (2, 3).

The measurement system consisted of a chromatograph Carlo Erba 8035 with a column DB-5, 60m, and high resolution mass spectrometer Autospec-Ultima (10000-12000) (2).

Results and Discussion

The results of PCDD/Fs determination on environmental objects and basic indices of measurement quality control depending from isomers are given in Tables 1 - 3.

Table 1. Parameters of analytical determination.

Objects	MDL	% of extraction	Sample	Error, %
River water (filtrate)	0.1-1 ppq	45-100	1L	3-17
Sewage (filtrate)	1-2 ppq	75-115	0.5L	5-15
Sediment on filter	3-8 ppt	85-97	0.1-0.2 g	2-10
Soil	0.1-1 ppt	65-95	2 g	3-17
Ground sediments	0.5-3 ppt	87-100	2 g	3-17
River fish	0.7-4.2 ppt	80-97	30 g	5-20
Whole blood	0.5-3.7 ppt	67-110	40 ml	4-25
Breast-milk	1-4.8 ppt	69-98	50 ml	3-20

For processing the results of analyzing the samples containing PCDD/Fs at the detection limit we used ½ MDL for calculations.

Table 2. Human exposure.

PCDD/PCDF	Human blood, pg/g lipids		Breast-milk, pg/g lipids		Fish, pg/g lipids
	SWC workers n=20	Control n=20	Industrial region Ezhva n=6	Syktyvkar, background n=10	
2378-TCDD	10.78	13.7	14.89	6.77	127.4
12378-PnCDD	8.96	ND(5)	9.43	2.89	7.3
123478-HxCDD	7.0	ND(5)	2.49	7.21	6.19
123678-HxCDD	9.0	ND(5)	3.83	3.63	17.23
123789-HxCDD	5.68	5.4	1.57	2.37	3.06
1234678-HpCDD	26.02	12.8	4.7	10.26	6.48
OCDD	161.2	72.0	24.51	58.56	33.2
2378-TCDF	6.0	7.4	2.31	1.30	73.45
12378-PnCDF	18.40	5.7	1.72	1.57	47.3
23478-PnCDF	21.31	13.4	1.01	10.05	52.3
123478-HxCDF	48.54	ND(7)	4.37	7.21	15
123678-HxCDF	14.90	ND(5)	2.23	3.60	4.61
123789-HxCDF	21.68	ND(1)	0.56	1.25	7.32
234678-HxCDF	13.94	ND(4)	1.0	1.68	3.75
1234678-HpCDF	27.33	10.6	2.45	4.06	19.26
1234789-HpCDF	15.5	3.3	0.37	0.74	1.52
OCDF	21.49	13.2	0.13	2.59	27.61
TEQ, PCDDs	**17.88**	**17.9**	**20.47**	**9.7**	**133.79**
TEQ, PCDFs	**22.54**	**8.54**	**1.64**	**6.7**	**39.21**
TEQ, PCDD/Fs	**40.42**	**26.44**	**22.14**	**16.4**	**173.0**

Table 3. Environmental levels.

PCDD/Fs	River water at the site of sewage discharge, pg/l		SWC sewage water, pg/l	Ground sediments, ng/kg	City soil, ng/kg	Industrial region soil, ng/kg
	up to	after				
2378-TCDD	ND(0.6)	3.56	313.2	ND(0.08)	0.19	0.15
12378-PnCDD	ND(0.6)	4.8	5.28	ND(0.07)	ND(0.6)	ND(0.1)
123478-HxCDD	ND(0.3)	2.8	1.5	ND(0.1)	0.18	ND(0.03)
123678-HxCDD	ND(1.0)	16.37	3.89	ND(0.1)	0.08	0.17
123789-HxCDD	ND(0.6)	3.14	1.5	ND(0.1)	0.09	0.13
1234678-HpCDD	2.25	2.51	12.16	0.19	1.24	0.98
OCDD	12.5	10.9	92.36	1.11	7.15	5.72
2378-TCDF	ND(0.7)	10.17	415.54	ND(0.07)	0.5	0.26
12378-PnCDF	2.43	9.49	19.56	0.14	0.29	0.13
23478-PnCDF	3.32	1.92	15.9	0.10	0.29	0.34
123478-HxCDF	6.75	18.31	29.94	0.34	0.69	0.38
123678-HxCDF	1.12	2.86	8.26	0.17	0.28	0.2
123789-HxCDF	1.59	3.45	9.50	ND(0.08)	0.25	0.17
234678-HxCDF	0.89	1.81	8.40	ND(0.05)	0.24	0.18
1234678-HpCDF	3.08	ND(2)	14.86	0.42	1.17	0.78
1234789-HpCDF	1.33	ND(2)	6.64	ND(0.08)	0.22	0.17
OCDF	1.50	3.43	18.66	0.36	2.14	1.72
TEQ, PCDDs	**1.12**	**8.31**	**316.67**		**0.54**	**0.25**
TEQ, PCDFs	**2.97**	**5.19**	**56.34**		**0.38**	**0.32**
TEQ, PCDD/Fs	**4.09**	**13.50**	**373.0**	**0.27**	**0.92**	**0.57**

River and waste water

In water samples taken from the river Vychegda upstream the place where its water is mixed with SWC waste water only dioxins Cl_7-Cl_8 are registered. Rather a high content of furans Cl_5-Cl_7 in the samples after mixing with waste water are defined. This group of compounds provides 72% of the sample toxicity and they are adsorbed by suspended solid particles. I-TEQ increases from 4.1 pg/l to 9.9 pg/l.

Waste water sampled from the purified waste water contained 88.5 mg/l of suspended solid particles on which 90% of I-TEQ was determined. The main isomers in the sample were TCDD, TCDF, PnCDF (in the ratio of 1:1.5:0.2). Subsequent additional purification (ponds, aerators) reduces PCDD/Fs content to 72.1 pg/l, mainly due to reducing the content of solid particles.

Bottom sediments, soil

Bottom sediments were sampled in the river 5 km downstream the place of SWC waste water discharge at 3 points spaced by 150 m along the water-way from the depth of 3.9-5.6 m. The samples consisted of humid sand and PCDD/Fs content was extremely low - 0.27 ngTEQ/kg of dry weight. Probably the river sandbed in the place of sampling did not allow to register the consequences of waste water discharge.

The soil samples in Syktyvkar and in the whole industrial area contain less than 1 ng/kg of dry weight. This low for an industrial area concentration of PCDD/Fs testifies to the absence of air pollution sources.

Human biological tissue

A pool sample of whole human blood taken from 20 donors living in Syktyvkar was given by the Blood Transfusion Station. The samples were taken by 10 ml from a person. Men at the age of 25-40 years, 78-80 kg of weight and 175-178 cm of height served as donors.

The background level for Syktyvkar was 40.4 pg/g of lipids what is by 2 times above the level considered as background for Russia: 17.23 pg/g of lipids (S-Petersburg, Baikalsk, Ufa) (4). The level of 40.4 pg/g of lipids for the population of Syktyvkar indicates to the presence of dioxin contamination sources, particularly with high share of penta-furans.

A control group for comparison consisted of 20 donors living in a "clean" forest area. The donors were of the same sex and with the same physiological parameters as those in Syktyvkar. I-TEQ of the pool sample was 26.4 pg/g of blood lipids. The background sample of breast milk of Syktyvkar women presented a pool sample of 10 healthy women with no occupational exposure. It was 16.4 pgTEQ/g of lipids.

All requirements of the WHO for sampling were observed: all donors were primiparas, they were permanent inhabitants of the region, breast milk was sampled within the period from 2 weeks to 2 months after the child birth, etc. A compete form recommended by the WHO was filled in for each donor.

The second sample was collected as a mean sample of breast milk from 6 women working at SWC (Ezhva district). The same requirements were observed as for the background sampling. I-TEQ of the pool sample was 22.1 pg/g of lipids.

As it is seen from Table 3, this sample apparently has traces of dioxin contamination (the content of 2,3,7,8-TCDD by 2 times exceeds that of the control group in Syktyvkar). A triple excess of 1,2,3,7,8-PnCDD as compared to the reference group was also defined.

Fish

A mean sample of freshwater fish contained 173 pg/g of lipids. This level is by 2 times above the norm for Russia (88.0 pg/g of fat for the eatable part of fish) and this confirms a probable contamination source – the water system of Syktyvkar.

Thus in the Republic of Komi the fact of PCDD/Fs contamination both of the environment and of human being was stated. Industrial waste waters of SWC discharged into the river serve as a contamination source.

Acknowledgements

This research was carried out by the initiative of the Centre of Sanitary and Epidemiological Control and financed by the budget of the Republic.

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