THE LEVEL OF PCDD/Fs POLLUTION IN THE ENVIRONMENTAL OBJECTS FROM THE PLACES OF MILITARY OPERATIONS IN THE REPUBLIC OF YUGOSLAVIA

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Introduction

There is rather a strong possibility of PCDD/Fs environmental pollution as a result of industrial failures, fires and oil products burning. During the military action in Yugoslavia in 1999 as a result of NATO air force point bombardments many oil refineries and railway stations were destroyed including railway cars with chemicals. Products of burning including toxic PCDD/Fs and PCBs formed in explosions and accompanying fires were spreading onto the residential areas of cities creating environmental and public health hazard. In the Environmental Research & Protection Centre of the Republic of Bashkortostan determination of toxic PCDD/Fs isomers was carried out in ten samples of some environmental objects: water, soil, bottom sediment and technical products. The substances were sampled in the city of Panchevo from the territory of the chemical plant "Azotara" and oil chemical complex "Petrochemistry" destroyed as a result of bombardments. The samples were taken by representatives of the Ministry of Civil Defence and Emergencies of the Russian Federation in July 1999.

Methods and Materials

Table 1 gives a brief description of samples and places of sampling. The samples were dried to the constant weight. PCDD/Fs concentration is given for the dry weight of the sample. Water samples were extracted with benzene and the extracts were purified by column chromatography with the use of SiO_2, Al_2O_3 and Carbopac-C/Celite 545. A filter with suspended solids was extracted in a Soxhlet apparatus with a mixture of methylene chloride and hexane. Soil and bottom sediment samples were extracted with a mixture of methylene chloride and acetone in an ultrasonic pot then humidity and ash content were determined. The composition of the product was not identified.
PCDD/Fs quantitative analysis was performed by the method of HRGC/HRMS in compliance with 1613 US EPA methods with the use of highly effective capillary column DB-5 MS (60 m) and a high resolution mass-spectrometer Autospec-Ultima, Micromass. The modes of chromatography and mass spectre registration were similar to those described earlier[1].
For toxicological assessment of the samples pollution with PCDD/Fs the scale I-TEQ was used.
Duplicate and blank experiments on model matrixes were performed for all the samples. All procedures of the four-level quality control of the analysis specified by the method EPA 1613 were also carried out.
The degree of recovery made 43-116%, MDL made from 0.04 ppt (TCDD) to 0.9 ppt (OCDD). In case of a high level of the sample pollution dilution of the obtained extracts was performed.

Table 1

Characteristics of the samples taken from the destroyed objects (sampled in July 20-22,1999)

Code	Place of sampling	Sample characteristic
J-1	Oil complex "Petrochemistry", destroyed shop of transformers	Water with sediment (0.02%)
J-2	Channel, waste water, oil complex "Petrochemistry"	Water with sediment (4.9 %)
J-3	Chemical plant "Azotara", masut (black oil) spill out of destroyed cisterns on railways	Soil, humidity - 8,8 %
J-4	The city of Panchevo, the area of the city hospital, downwind side of fires	Soil, humidity – 16.4 %
J-5	Channel containing the products of destroyed store houses of the chemical plant "Azotara"	Organic substance, humidity – 40.4 %, ash content – 34 %
J-6	The city of Panchevo, the area of a school, upwind side of fires	Soil, humidity – 8.3 %
J-7	The area of the destroyed chemical plant "Azotara"	Soil, humidity – 18.9 %
J-8	Oil complex "Petrochemistry", the place of fire, a train of cars with PVC monomer	Soil (0-20 cm, humidity - 9.7%)
J-9	Oil complex "Petrochemistry", the place of fire, a train of cars with PVC monomer	Soil from the depth of 25 cm, humidity-10.8%
J-10	Oil chemical complex "Petrochemistry", a destroyed shop for PVC production	Bottom sediment, humidity-95 %

Results and discussion

The results of PCDD/Fs determination are given in Tables 2 and 3.

Table 2

I-TEQ PCDD/F in the samples,

Code	Object	I-TEQ	Code	Object	I-TEQ
J-1	Water	15.2 pg/L	**J-6**	Soil	0.4 ng/kg
J-2	Water	9.4 pg/L	**J-7**	Soil	14.7 ng/kg
J-3	Soil	0.9 ng/kg	**J-8**	Soil (0-20 cm)	12.3 ng/kg
J-4	Soil	0.4 ng/kg	**J-9**	Soil (>25 cm)	140.2 ng/kg
J-5	Organic substance	2.5 ng/kg	**J-10**	Bottom sediment	3716.0 ng/kg

Table 3

Concentration of PCDD/Fs isomers in the samples from the areas of military operation

PCDD/ PCDFs	J-1*, pg/l	J-2*, pg/l	J-3, pg/g	J-4, pg/g	J-5, pg/g	J-6, pg/g	J-7, pg/g	J-8, pg/g	J-9, pg/g	J-10, pg/g
2378-TCDD	1.9	1.2	0.04	0.04	0.1	0.04	0.3	0.2	1.6	4.5
12378-PnCDD	1.1	2.1	0.3	0.1	0.4	0.1	1.0	2.4	18.7	33.4
123478-HxCDD	1.3	1.6	ND(0.1)	0.07	0.4	0.07	ND(0.1)	ND(0.2)	10.0	29.7
123678-HxCDD	0.9	1.8	0.2	0.05	0.1	0.05	0.7	1.2	11.2	58.8
123789-HxCDD	1.0	1.8	0.3	0.1	0.2	0.1	0.51	0.9	9.3	50.0
1234678-HpCDD	6.0	3.6	2.1	1.4	0.7	1.4	6.8	17.2	111.2	591.4
OCDD	21.5	16.6	14.6	13.4	3.3	13.3	12.1	3.4	255.0	2000
2378-TCDF	19.3	12.2	0.8	0.3	0.5	0.4	21.9	8.6	45.7	115.9
12378-PnCDF	6.9	6.4	0.3	0.1	0.3	0.1	5.0	8.3	53.0	396.4
23478-PnCDF	11.0	5.4	0.7	0.2	1.3	0.2	17.2	14.0	100.7	233.3
123478-HxCDF	19.8	13.6	0.7	0.2	2.2	0.2	10.4	0.2	236.7	3512
123678-HxCDF	5.9	3.6	0.4	0.2	1.0	0.1	4.8	0.1	160.3	1902
123789-HxCDF	7.5	1.9	0.2	0.1	0.8	0.1	2.7	0.3	56.1	420
2346678-HxCDF	4.8	2.6	0.3	0.2	1.2	0.1	5.8	0.2	111.1	561.2
1234678-HpCDF	50.3	63.1	1.6	0.6	6.4	0.2	12.4	163.6	898.2	240000
1234789-HpCDF	9.2	9.3	0.2	0.2	1.1	0.8	3.0	22.0	132.8	2571.8
OCDF	75.8	108	1.5	1.1	9.3	0.2	7.1	245.6	809.8	460000
I – TEQ	**15.2**	**9.4**	**0.9**	**0.4**	**2.5**	**0.4**	**14.7**	**12.3**	**140.2**	**3716.0**

ND = ½ MDL. * - the sum total of the concentrations in the filtrate and on the filter.

To analyse the data we have used Russian environmental and hygiene standards for dioxin and congeners content in the environmental objects (I-TEQ). Approximately a safe level of the content in soil is 0.33 ng/kg, in bottom sediment – 9 ng/kg, permissible concentration in potable water, ground and surface waters, in water intakes – 20 pg/l. In the Republic of Bashkortostan PCDD/Fs safe level in water is 1 pg/l. In some other countries other permissible PCDD/Fs concentrations are allowed: in chemical products including pesticides - 1×10^{-6} g/kg, in industrial wastewater -5×10^{-5} g/l. Comparing the found data on analysis of water and soil from places of military operation in the Republic of Yugoslavia and the above given environmental – hygiene standards one can see the following. PCDD/Fs content in water samples is lower than it is specified by Russian standards but it by 100-500 times exceeds the norms of European countries. It is common that in surface and drinking water of conditionally clean areas PCDD/Fs content as a rule does not exceed 1 pg/l. In water samples from the territory of the chemical plant "Petrochemistry" there is a considerable amount of suspended solids present. Pollution of the sample depends on the content of PCDD/Fs on these particles. In the water sample from the channel PCDD/Fs (J-2) content does not exceed 9,5 pg/l, the content of suspended solids being equal to 4.9%. In the sample from the destroyed transformer shop (J-1) PCDD/Fs level is over 15 pg/l with the content of suspended solids equal to 0.02%. Soil samples from the city of Panchevo, from the city hospital and school contained PCDD/Fs at the levels of 0.4 ng/kg and 1.3 ng/kg, i.e. there is threefold excess in the second case. Isomer spectre of pollution points to the process of burning.

The destroyed industrial sites of the plants "Petrochemistry" and "Azotara" may be ranked as extremely polluted zones. Isomer spectre of soil samples is characterised by high PCDFs content, a large amount of PCBs is present what may be caused either by technological processes of the plant or by the processes of uncontrolled PCBs burning. Bottom sediments are extremely hazardous in terms of probable transfer over the area. Special measures are required for conservation of polluted soil and bottom sediments. The research has shown that considerable PCDD/Fs pollution both of urban and industrial areas may be detected and stated by the presented samples. Most likely there is an active source of strong PCDFs and PCBs pollution because considerable concentrations of these compounds are present practically in all samples. As it has been shown by the results of our studying the pollution of industrial sites of petrochemical complexes in Russia similar to those in Panchevo such a considerable dibenzofurans content is not characteristic for them [2]. However these compounds accompany the process of PCBs burning and their presence may be caused by military operations (explosions, fires) and by burning chemical products.

It should be noted that this research does not allow for making an exact conclusion about the origin of dioxin pollution. This requires a more detailed examination of the area and especially of the population living in the area of exposure (blood, fat, human milk), rescue teams eliminating damage consequences, military men and other risk groups.

Research of PCDD/Fs determination should also be carried out in the areas of Yugoslavia that were not attacked for determination of the true background level in this country. The authors failed to find in literature any data for Yugoslavia on the background levels of dioxins in environmental and biological objects though there is such data almost for all European countries.

References

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2. Amirova Z., Kruglov E., Loshkina E., Chalilov R. Organohal. Comp., 1996, 32, 107.