DIOXIN CONTAMINATION OF SNOW AND ATMOSPHERIC AIR IN KRASNOYARSK

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Introduction

It is known, that atmospheric transfere is one of the main paths of dioxins widespreadning. Therefore dioxin content in atmospheric air is regulated in many countries. Maximal allowed level of dioxins in air in USA is 0,02 pg/m^3, in Italy 0,04 pg/m^3, in the Netherlands 0,024 pg/m^3, in Russia 0,5 pg/m^3 [1].

The main sourses of dioxin pollution of atmospheric air are industrial gas exhausts, combustion products of fuel, industrial and municipal wastage, exhaust gases of internal combustion engines.

Average concentration of dioxins in atmospheric air of cities is 0,001-1 pg/m^3, at transferring from center to suburbs it is moderated from 1,4 to 0,4 pg/m^3 [1]. In atmospheric air samples in Chapaevsk averaged per year dioxin concentration (in I-TEQ) in polluted sites was 0,34 pg/m^3 [2]. In atmospheric air of Novodvinsk the dioxin concentration was 43,8 pg/m^3 [3].

The concentrations of dioxins in atmospheric air in cities Ufa, Salavat, Sterlitamak are 0,2-0,5 pg/m^3 [4], that is comparable with dioxin concentration in Chapaevsk. Snow samples give the averaged pattern of contamination for a rather long time. In snow samples from Ufa in March, 1997 the content of dioxins was 3-400 pg/L and in territory of the Chimprom it exceeded 600 pg/L [4]. In other cities of Russia the content of dioxins in snow samples was 0,2-30 pg/kg [5].

We studied dioxin contamination of snow cover in Krasnoyarsk sity. Snow was sampled on March 3-5, 1998. Blanket of snow had thickness 12-35 sm and laid about 0,356 years. 32 samples (1 sample on 10000 km^2) were selected. On the base of some assumptions dioxin deposition rates were evaluated and mean PCDD/PCDFs concentration in atmospheric air.

Experimental

Snow samples were melted, to water (volume about 5 L) isotope labelled standards were added. Samples were filtrated through the thin quartz fibre filter diameter of 90 mm under small vacuum.

The filters with particles were crumbled up and extracted in special extractor by 250 mL mixture hexane-dichloromethane (1:1) at temperature ~ 70°C or by 250-300 mL mixture isooctane-dichloromethane-toluene (85:10:5) at temperature ~ 100°C.

Extracts were cleaned as was described elsewere [6].

To prepared extract 1 ng internal standard - 2-fluoro-6,7,8,9-tetrachlorodibenzo-p-dioxin and 10 mcL n-tridecane were added and the extract was analysed by GC-HRMS on the instrument Finnigan MAT 95 XL..

Results and discussion

PCDD/PCDF concentrations in snow samples are shown in the Table 1. They are within limits from 38 up to 1470 pg/L, the mean value is 289 pg/L, and median - 149 pg/L. For comparison in Ufa in 1997 PCDD and PCDF content in snow samples was 3-400 pg/L, and in the "Chimprom" factory - 900 pg/L.

A high content 2,3,7,8-TCDD in some samples was found, maximal value achieved 1,44 ng/L. The rather high concentration 2,3,7,8-TCDD was observed also in snow samples collected in Ufa near automobile road with hard traffik [4].

2,3,7,8-TCDF also was found in the majority of the samples, in some samples its concentration reachs rather major values - about 0,5 pg/L. As a rule, OCDD in high concentration is present in all samples. High concentration OCDD, HpCDD and OCDF is characteristic for burning of chlorinated materials [1,7].

Thus, the presence of HpCDD, OCDD, PCDFs in snow samples can be provoced by exhaust gases of automobile engines working on leaded gasoline, combustion of wastage etc. However, they can be formed as well as a result of industrial processes mainly metallurgical.

Reviewing of the main processes of PCDD/PCDFs deposition from atmosphere [8,9] has reduced in following results (Tab.2). Approximately 15-20 % all PCDD/PCDFs in atmosphere is decomposed due to photochemical and chemical reactions, the remaining 80-85% precipitate on a surface by dry and wet precipitation.

In Tab.4 the estimated values of precipitation rates of PCDD/PCDFs from atmosphere are presented. They are within the interval from 5,57 up to 254,6 ng/m^2/year at a medial value 49,2 ng/m^2/year and standard deviation 65,5 ng/m^2/year. Use of lognormal distribution gives the estimate of medial rate of precipitation PCDD/PCDFs in all Krasnoyarsk territory 26,2 ng/m^2/year and dioxin load 8,63 g/year.

The medial concentration PCDD/PCDFs in atmospheric air was estimated as 0,38 pg/m^3 (maximal allowed level is 0,5 pg/m^3), interval of values - from 0,08 up to 3,71 pg/m^3). In 12 sampling sites calculated concentration was exceeded maximal allowed level.

Conclusion

The rather high concentration PCDD and PCDFs in snow samples testifies to a high content them in free air. Hence, there are stationary sourses of emission in an atmosphere of these contaminats and their atmospheric transportaition. The estimated medial rate of precipitation PCDD/PCDFs in Krasnoyarsk is 26,2 ng/m^2/year and dioxin load 8,63 g/year. Calculated PCDD/PCDFs concentration in atmospheric air is 0,38 pg/m^3. This value in 3-8 times exceeds the relevant estimates for the European industrial regions.

The congener profile of PCDD and PCDF is the evidence of several different dioxin emission sources occuring. Firstly, these are combustion processes: burning of solid fuel, combustion of municipal and industrial wastes, exhaust gases of automobile engines, fires, etc. Secondary, these are gas exhausts of metallurgical plants, in particular of aluminium industry.

References

1. Maystrenko V.N., Khamitov R.Z., Budnikov G.K., Ecologo-analytical monitoring of ecotoxicants, M., "Khimia", 1996, p.331-332.
2. Report on the project "The complex of top-priority actions for impouving of ecogical situation in Chapaevsk", 1994, Tayphoon, Obninsk.

3. Report on the project "Evaluation of dioxin pollution and finding of the emission sources in Arckhangelsk and Arckhangelsk region", CNEP, Mc-Arthurs foundation, Ministry of the Nature PF, 1993-1994. 80 p.
4. Amirova E.K., Kruglov E.A., The situation with dioxins in Respublika Bashkortostan, Ufa, 1998, p.14-15.
5. Grosheva E.I., Danilina A.E,. Tychkin L.V., An estimation of pollution of the territory of Russia by dioxins and relative compounds, in "Dioxins – superecotoxicants of the XX century. The Federal project", N.2, M., 1998, p.20-76.
6. Soyfer V.S., Soboleva E.I., Brodsky E.S., Klyuev N.A, Improved sample preparation procedure for PCDD/PCDF determination in the environment using modified carbon columns, Jornal of Analytical Chemistry(Rus), V.50, N.3, 262-266, 1995.
7. Klyuev N.A., Soyfer V.S., Korotkov M.G., Brodsky E.S., Gotlib E.M., Yufit S.S., Investigation of PCDD, PCDF and PAH evolving from combustion of linoleum.- Organohalogen Compounds, Vol.36, pp.317-320.
8. 8. Koester J.C., Wet and dry deposition of chlorinated dioxins and furans, Environ. Sci.Technol. – 1992, v.26, N.7, pp.1375-1382.
9. Eitzer B.D., Hites R.,Atmospheric transport and deposition of polychlorinated dibenzo-p-dioxins and dibenzofurans. Environ.Sci.Technol. – 1989, v.23, N.11, pp.1396-1401.

Table 1

PCDD and PCDF concentration in snow samples (pg/L)

№	Component	Min	Max	Av	Med
1	2,3,7,8-TCDD	8,9	1440,7	152,4	44,9
2	1,2,3,7,8-PeCDD	7,0	398,1	55,0	30,2
3	1,2,3,4,7,8-HxCDD	15,5	154,5	69,2	72,2
4	1,2,3,6,7,8-HxCDD	16,0	608,8	109,6	40,3
5	1,2,3,7,8,9-HxCDD	28,1	278,0	125,2	69,4
6	1,2,3,4,6,7,8-HpCDD	18,9	448,6	151,8	117,4
7	OCDD	123,4	62604,1	5979,0	821,75
8	2,3,7,8-TCDF	48,0	808,9	282,6	234,7
9	1,2,3,7,8-PeCDF	23,4	376,7	97,2	75,0
10	2,3,4,7,8-PeCDF	18,5	273,3	92,1	80,3
11	1,2,3,4,7,8-HxCDF	80,6	458,2	257,5	249,2
12	1,2,3,6,7,8-HxCDF	62,8	508,9	181,8	116,0
13	2,3,4,6,7,8-HxCDF	69,3	675,6	268,5	201,8
14	1,2,3,7,8,9-HxCDF	24,8	131,3	62,7	32,0
15	1,2,3,4,6,7,8-HpCDF	36,7	336,0	166,5	199,8
16	1,2,3,4,7,8,9-HpCDF	84,7	654,4	422,1	527,2
17	OCDF	65,3	1769,6	349,8	171,0

Table 1 (continuation)

№	Component	Min	Max	Av	Med
18	Сумма др.TCDD	17,9	890,3	211,6	96,9
19	Сумма др. PeCDD	29,7	558,2	146,7	91,7
20	Сумма др. HxCDD	29,8	3051,4	370,9	116,8
21	Сумма др. HpCDD	33,7	459,2	150,7	77,3
22	Сумма др. TCDF	48,7	3886	741,3	351,1
23	Сумма др. PeCDF	21,2	963,9	310,9	216,9
24	Сумма др. HxCDF	26,3	920,4	243,1	144,6
25	Сумма др. HpCDF	107,8	339,8	223,8	223,8
	I-TEQ	**41,6**	**1472,1**	**315,6**	**188,2**

Table 2
Contribution of main processes of removing of PCDD and PCDF from atmosphere

Process	Characteristic time of removing of PCDD and PCDF from atmosphere – t, days	1|t (day^{-1})	Contribution, %
Photolysis	42 (PCDD) 78 (PCDF)	0,0238	5,2
Chemical reactions	17 (PCDD) 50 (PCDF)	0,0588	13,0
Dry deposition	3	0,3333	73,6
Wet deposition	29	0,0370	8,2
Sum		0,4529	100,0