MONITORING OF PCDD/FS AND PCBS IN SOIL OF RUSSIA CITIES (FROM BRYANSK TO VLADIVOSTOK)

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Introduction

Soil is a convenient matrix for preliminary assessment of POPs pollution in large areas due to easy sampling procedure and possibility of sample archiving without special efforts. However natural heterogeneity of the matrix, dependence of adsorption properties on the content of organic hydrocarbon and component composition of samples are complicating moments. The term «urban agglomeration soil» is rather conditional because soil for planting may be brought from different areas and the impact of automobile transport exhaust and local PCDD/Fs pollution sources adversely affect the situation.

Samples of background territories are more representative when we speak about biosphere reserves included into the global monitoring network. However for localising PCDD/Fs emission sources it is very often required to compare soil pollution in urban centres and in rather distant areas.

For cities and background territories in Russia there is a limited but constantly replenished data bank on PCDD/Fs content in soil [1]. Carried out according to a uniform method, this research needs expansion to new territories of Russia.

Concerning PCBs soil pollution the situation is more complicated. From 1976 and for many years there existed a system of global background monitoring in the former Soviet Union. There were 12 observation stations in biosphere reserves situated in forest ecosystems of the European part of the USSR, in mountainous forests of the Western Caucasus, in steppes of the Volga River estuary, in steppe part of Northern Kazakhstan, in deserts and mountains of Central Asia, in forests of Transbaikalia and in Far - Eastern forests. The main objects of studying their chlororganic compounds were isomers of hexachlorocyclohexane, DDT and its metabolites. PCBs (components of arochlor 1254) were also included into the list of primary pollutants but they were analysed only at some stations by the method of GC. In the soil of the largest of them, Astrakhan and Caucasus biosphere reserves, PCBs levels were 2-20 μg/kg in the 80s.

Alongside with soil analysis PCBs were determined in atmospheric precipitation, vegetation, bottom sediments, surface waters, in tissues of wild animals. In the Bashkirian biosphere reserve situated in the South Urals PCBs determination was not performed.

Later research carried out on the Barents sea coast, Lake Baikal, in Irkutsk and Samara regions of Russia (soil, snow, fat tissue) included the measurement of PCBs group composition or indicator PCBs (IUPAC ## 28, 52, 100, 118, 138, 153, 180). Among them only #118 enters the group of DLPCBs what does not give any possibility of comparing pollution levels, tracing the chain of biomagnification, animal and human food chains[2-5]. Sometimes the number of the analysed PCB isomers exceeded 60 but only 2-3 of them were toxic[3,6]. Statistic data obtained in the course of realising the AMAP project on PCBs inventory in the Russian Federation give only an approximate picture; many regions didn't give any information concerning PCBs-containing equipment and waste[7].

This paper presents first experimental results of complex PCDD/Fs and DLPCBs monitoring in soil of some regions in Russia.

LEVELS IN ABIOTIC COMPARTMENTS

Methods and Materials

Soil sampling in cities and in background regions served as an object for study. PCDD/Fs were determined by the method USEPA 1613 and DLPCBs (IUPAC ## 77,81,105,114,118,123,126,156,157, 167,189) by the USEPA 1668 A.

The area of soil sampling was from Bryansk region in the West to Chukot Peninsular and the city of Vladivostok in the East of Russia. Table 1 gives a brief description of samples and places of sampling.

Table 1.

Code	Place of sampling	Sample characteristic
S-1	Bashkirian biosphere reserve, the South Urals	N=5; background
S-2	The city of Ufa, the South Urals	N=32; I, II
S-3	Eastern Siberia, background region	N=2; background
S-4	The city of Chita, Eastern Siberia	N=11; IV
S-5	Background region, the Northern Urals	N=2; background
S-6	The city of Ukhta, the Northern Urals	N=3; II
S-7	The city of Vladivostok, Far East	N=1; III, IV, 500 m from MWI
S-8	Bryansk region, Western Russia	N=3; background
S-9	The city of Kurgan, West Siberia	N=1; III, IV
S-10	Chukot Peninsular	N=1; background

I - industry of organic synthesis, production of chlorine, chlorine-containing pesticides, production of 2,4,5-T (earlier); II - oil chemistry, oil refining; III - mechanical engineering, transport; IV - heat-and-power engineering.

The samples (20g of soil from background areas or 3 g of urban soil) were dried to the constant weight. PCDD/Fs concentration is given for the dry weight of the sample. Soil samples were extracted with a mixture of methylene chloride and acetone in an ultrasonic pot and the extracts were purified by column chromatography with the use of SiO_2, Al_2O_3 and Carbopac-C/Celite 545. PCB determination was made of a separate sample (1-3 g), the scheme of extraction was the same as for PCDD/Fs, extract purification was carried out with the use of acid silica gel and activated Florisil column. The degree of recovery made 43-116 %, MDL made from 0.04 ppt (TCDD) to 0.9 ppt (OCDD) and 0.5-1 ppt for PCBs. Duplicate and blank experiments on model matrixes were performed for all samples.

All used standards for calibration, purification, labelled surrogates of all analysed compounds, inner standards of both methods were received from CIL and Wellington.

The measuring system consisted of a chromatograph Carlo Erba 8035 with a column DB-5 MS, 60m, and a mass spectrometer Autospec - Ultima (10000). The laboratory of the ERPC has successfully participated in the 5th round of international intercalibration research carried out by the University of Umee, Sweeden, 1999 (PCDD/Fs and DLPCBs in soil).

Results and discussion

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

PCDD/Fs pollution level of background territories (S-1, S-3, S-5, and S-10) is 2-5.4 pg/g d.w. (0.15-0.59 pg/g TEQ) and 0.3-1.0 ng/g d/w/ DLPCBs (0.09-0.32 TEQ PCBs). A sample from a rural area of Bryansk region (S-8) is out of this row. In this sample there is a high content of low-chlorinated

Table 2. TEQ PCDD/F and PCBs in soil, pg/g d.w.

Code	TEQ, PCDD/Fs	TEQ, PCBs	Code	TEQ, PCDD/Fs	TEQ, PCBs
S-1*	0.15	0.09	S-6	1.19	1.51
S-2	3.19	0.34	S-7	437.7	31.3
S-3*	0.27	0.27	S-8*	1.95	0.24
S-4	1.94	1.92	S-9	3.69	0.36
S-5*	0.30	0.32	S-10*	0.59	0.09

*- background, rural area

isomers, probably due to the use of 2,4-D herbicide[8], and it should not be considered as s background sample.

Urban soil (S-2, S-4, S-6, and S-9) is polluted unevenly: 32.9-146 pg/g d.w. PCDD/Fs (1.19-3.69 TEQ PCDD/Fs) and 1.8-6.4 ng/g d.w. PCBs (0.34 -1.92 TEQ PCBs).

TEQ PCDD/Fs in Ufa and Kurgan are practically equal. However, if in Ufa the main contribution is made by 2378-TCDD (the result of phenoxyherbicide production) then in Kurgan it is 23478-PnCDF, pollution souses are not stated.

A soil sample from the city of Vladivostok taken within the city boundaries at a distance of 500 m from MWI occupies a special place. PCDD/Fs content in the sample reaches 7773.6 pg/g d.w. (437.7 pg/g TEQ). It was determinated in the course of research supported by the USEPA grant 82769701[1]. We have supplemented these data with determination of PCBs in the same sample. PCBs content was also high: 26 ng/g d.w. (31.3 pg/g d.w. TEQ PCBs). The pollution is caused by a long-time exposure to emission of municipal waste incinerator. The MWI is processes over 450 tons of waste per day. The waste gas is not purified, only fly ash is caught. The MWI waste (58.5 tons annually) is not utilised.

References

1. Yufit S., Grosheva E., Adibi J. Organohal. Comp., 2001, 50, 401
2. Mamontova E, Mamontov A, Matorova N, Tarasova E, Chuvashev U. Org. Comp., 1977, 32, 72
3. Mamontova E., Mamontov A., Tarasova E., McLachlan M. Organohal. Comp., 1998, 38, 131
4. Savinov V., Savinova T., Dahle S., Matishov G., Iljin G., Organohal. Comp., 1999, 43, 409.
5. Grosheva E., Beim A., Renzoni A., Bobovnikova T. Organohal. Comp., 1995., 26., 441.
6. Korrick S., Altshul L., Revich B., Bobovnikova T., Chernic G. Org. Comp., 1998., 38., 231.
7. Amap Report 2000:3 PBC in the Russian Federation: Inventory and proposals for priority remedial actions, ISBN 82-7971-008-6, Oslo, Moscow, 2000
8. Komogortcheva L., Prosyannikov E. Organohal. Comp., 1999, 43, 179.

Table 3. PCDD/Fs and PCBs in the soil samples from Russian region

PCDD/PCDFs	S-1 *	S-2	S-3*	S-4	S-5*	S-6	S-7	S-8*	S-9	S-10*
2378-TCDD	ND(0.05)	0.87	ND(0.03)	0.09	ND(0.08)	0.13	14.91	0.23	0.21	0.17
12378-PnCDD	ND(0.01)	0.16	0.09	0.37	ND(0.07)	0.17	114.21	1.26	0.33	1.71
123478-HxCDD	ND(0.03)	0.74	0.09	0.08	ND(0.05)	0.12	123.52	ND(0.4)	0.54	0.17
123678-HxCDD	0.12	ND(0.1)	0.06	0.03	0.1	0.15	196.47	0.5	0.88	0.24
123789-HxCDD	0.07	0.19	0.08	0.24	ND(0.01)	0.27	111.78	ND(0.4)	1.16	ND(0.1)
1234678-HpCDD	0.27	14.1	1.0	3.03	0.19	2.03	922.88	1.09	10.86	0.34
OCDD	0.62	81.1	2.5	15.2	1.11	20.21	1000.0	9.76	62.22	1.56
2378-TCDF	0.03	3.52	0.27	2.15	ND(0.07)	0.89	99.35	0.28	1.27	0.22
12378-PnCDF	ND(0.02)	1.3	0.23	1.02	0.14	0.52	113.21	0.3	0.84	0.02
23478-PnCDF	ND(0.05)	1.48	0.08	1.44	0.10	0.64	259.51	0.38	2.43	0.35
123478-HxCDF	0.12	2.07	0.17	1.17	0.34	0.86	224.39	ND(0.2)	2.92	ND(0.1)
123678-HxCDF	0.15	ND(0.1)	ND(0.05)	0.37	0.17	0.57	201.55	ND(0.1)	2.07	ND(0.1)
123789-HxCDF	ND(0.1)	1.4	0.07	1.3	0.08	0.34	85.06	ND(0.2)	1.45	0.21
2346678-HxCDF	ND(0.03)	1.42	0.08	0.89	ND(0.05)	0.67	208.16	ND(0.1)	2.66	ND(0.1)
1234678-HpCDF	0.09	15.7	ND(0.04)	3.96	0.42	11.35	9791.52	0.67	47.65	0.34
1234789-HpCDF	ND(0.1)	2.2	ND(0.1)	0.98	0.08	0.61	94.05	ND(0.1)	0.83	0.08
OCDF	0.31	8.6	0.5	0.6	0.36	4.44	213.02	0.1	7.78	0.64
33’44’-TCB (77)	4.2	10.2	2.4	260.2	28.6	13.2	1036.5	57	10.1	0.45
344’5-TCB (81)	3.4	15.4	9.9	40.0	ND(5)	65.4	87.6	13.9	42.4	2.2
233’44’-PnCB (105)	15.4	617.8	45.5	1742.7	27.9	968.4	3649	149	35.1	89.9
2344’5- PnCB (114)	5.4	52.8	3.4	117.4	42.4	55.2	392	1.9	0.45	0.1
23’44’5- PnCB (118)	245.1	1445.1	843	3682.4	105.1	2513.4	14900	457	1683.4	665.2
2’3455’-PnCB (123)	4.80	15.40	ND(0.3)	ND(1)	10.4	22.9	1254	23.1	2.1	0.54
33’44’5-PnCB (126)	0.40	0.80	ND(0.6)	10.7	2.4	ND(10)	279.3	0.9	1.46	0.02
2’44’5’-HxCB (156)	3.4	15.4	49.3	329.8	57.8	124.5	1264.3	129.8	24.8	8.79
233’44’5’-HxCB (157)	2.4	13.2	11.6	81.2	9.3	18.6	596	4.1	6.54	0.1
23’44’55’-HxCB (167)	6.3	26.4	19.9	134.5	16.4	31.8	2357	24.8	14.2	9.89
33’44’55’-HxCB (169)	1.1	1.08	0.2	0.6	ND(1)	ND(5)	13.5	ND(0.7)	0.9	0.1
233’44’55’-HpCB(189)	5.4	2.2	1.9	14.1	16.9	12.9	19.9	16.4	46.2	18.4
Total PCDD/Fs	2.17	135.0	5.4	32.9	3.7	44.9	7773.6	229.0	146.1	4.7
Total PCBs	307.3	2251.8	1026.4	6414.6	323.1	3841.3	26027	878.6	1872.5	789.8