Contamination of Vladimir region by PCDDs, PCDFs and PAH

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Introduction

Analysis of demographic situation in Vladimir and some sites in Vladimir region (e.g.Suzdal) clarified that there is a contribution of technogenic component amonght dyeness reasons. It was shawn [1] that PCDD/PCDF content in breast milk in Suzdal (Vladimir region) was 13,5 hg/g (TEQ) fat and PCB – 14,4 pg/g fat (TEQ), higher than in chemical industry region such as Salavat, Volgograd, Dzerjinsk.
Therefore an investigation of contamination of Vladimir region by PCDDs, PCDFs and PAHs was carried out. A number of samples of soil, air and foodstuffs (milk, butter) were collected in various sites which were suspiciously been contaminated and considered as background.

Material and Methods

Air samples were collected on thin silica fibers filters coated with vaseline. Internal standards, $^{13}C_{12}$-labelled dioxins, were applied on the filters before sampling. Air was passed through the filters with the rate 1.8 m^3/min during 3 hours. The filters were packed in polyethylenic bags and protected against light.
In the laboratory the filters were reduced in size and extracted with 400 ml toluene at 100°C. Extract was evaporated to vaseline, dissoluted in 100 ml hexane, 10 ml was taken for PAH determination and the rest passed through "multilayer" column with silica modified by acid and base. The column then was washed with 100 ml hexane, the eluate was passed through carbon microcolumn with 20 mg carbon FAS-MD on 200 mg celite. The column was washed with 20 ml hexane-dichloromethane (1:1, v/v), then eluated with 5 ml toluene in reverse direction at 80°C. The toluene eluate was diluted with hexane to 50 ml and passed through "multilayer" column, which then washed with 50 ml hexane. Combined eluates were loaded on column with Al_2O_3, which was washed 30 ml hexane, then 40 ml hexane-dichloromethane (95:5) and 50 ml hexane-dichloromethane (50:50). The last eluate was evaporated to 50 mcl and analyzed by GC-MS.

Soil and sediments were dried, grinded, added internal standards, placed into extractor and extracted with hot n-octane at temperature 100°C, pressure 2-3 atm and rate 5 ml/min. 10 ml was taken for the PAH determination and the rest was passed through "multilayer" column, then was clean-up on carbon microcolumn, "multilayer" column and column with Al_2O_3 as was described above.

To 150 ml milk internal standards, 150 ml acetone and 150 ml hexane are added mixed using homogenazer 3 min to homogenic mixture formation. To the mixture 105 g ammonium sulfate is added and is shaked to total dissolution. After layers separation (about 5 min) organic layer separated by decating and was clean-up on carbon microcolumn, "multilayer" column and column with Al_2O_3 as was described above.

To 10 g butter internal standards was added. Butter was dissolved in 200 ml hexane-acetone mixsture (1:1) and shaked some time for equilibrating. Solution was clean-up on carbon microcolumn with 10 ml toluene. 5 ml of eluate was taken for the PAH determination. The rest passed through "multilayer" column and column with Al_2O_3 as was described above.

Cleaned extracts were analysed using GC-MSHR for PCDD/PCDF and HPLC for PAH. Gas chromatograph Varian 3400 equipeed with silica capillary column 30mx0.25mm with stationary phase HP-5 and mass spectrometer Finnigan HSQ 30 were used. Column temperature was programmed from 160°C(1 min) to 220°C with rate 25°C/min and then to 270°C with rate 5°C/min. Molecular ions of PCDDs and PCDFs were registrated in MIS mode at resolving power about 6000.

Aliquot for PAH determination was cleaned up on basic alumina column. The basic alumina using is significant because it prevents a loss of some PAH, especially more light. An internal standard benzo(a)fluorene was added to the extract. The extract is loaded into column which is then washed by hexane, hexane-methylenechloride (5:95) and hexane-methylenechloride (50:50). The third fraction is evaporated to dryness, dissolved in 1 ml acetonitril and analysed for PAH by HPLC with fluorescent detection.

Liquid chromatograph HP 1090 with stainless steel column 250 mm x 4.0 mm filled with reverse phase sorbent Nucleosil-100-5C18 (5 mcm) and detector-fluorimeter HP 1046 was used for PAH determination.

Results and Discussions

Results of PSDD/PCDF determination in soil, air and foodstuff samples are presented in the Tab.2-3. Soil samples can be divided into tree groups on the level of PSDD/PCDF contamination. The lowest PSDD/PCDF content is in samples 10 (0,026 pg/g) and 18 (0,016 pg/g). These values can be accepted as background. PSDD/PCDF content in samples 4, 6, 8, 13, 14, 25-27 is in range 3-10 pg/g. These soils can be considered as not high level contaminated. At least in other soil samples PSDD/PCDF content is much higher - from 15-18 to 93 pg/g and in one sample, wall coating from cable production plant, it is reached 570 pg/g. In samples 7, 11, 12, 17, 28 PCDF content is relatively high that is typical for PCB technical mixtures.

PCDD/PCDF content in air sample collected in Suzdal (sample 5) is not so high – about 0,02 pg/m^3, in Vladimir (sample 9) and in Kolchugino (sample 16) it is some higher – 0,6-0,9 pg/m^3 (maximal allowed concentration is equal to 0,5 pg/m^3). Relatively high PCDD/PCDF concentration in atmospheric air indicates that there is a permanent source of these compounds and their atmospheric transport.

Butter samples can characterize an integral contamination. It is comparatively low in butter samples 21 and 22 from Suzdal and Vladimir (about 0,06 pg/g) and higher in samples 19 from Yurjev-Polskoy (1,3 pg/g) and Gorochovez (6,1 pg/g). Especially high PCDD/PCDF content in goat milk from the village Stary Dvor (sample 1) – 211 pg/g fat. Relatively high PCDF concentration in the milk and butter samples 1 and 20 points on possible contribution of PCB's used as transformers oils or additives to them.
High PAH contamination is observed in the samples from industrial areas (samples 12, 14, 28) and sites adjacent to roads with hard traffic (samples 6,27).

Table 1

List of samples collected in Vladimir region

№	Sample name, site of collection
1	Goat milk, Vladimir region, village Stary Dvor
2	Soil from pasture, region, Suzdal district
3	Soil from landfill, Vladimir city
4	Soil from pasture, region, Suzdal district, village Novo-Alexandrovo
5	Atmospheric air, Suzdal town
6	Soil from Bogolyubov meadow, village Bogolyubovo
7	Soil from municipal incinerator in Vladimir
8	Soil from agricultural firm in Vladimir
9	Atmospheric air in Vladimir
10	Soil from Ill's meadow, Suzdal town
11	Wall coating from cable plant in Vladimir
12	Soil from industrial incinerator in Vladimir
13	landfill of motor transport firm, Vladimir city
14	Soil from cleaning system, village Kusupovo.
15	Sediment from cleaning system Kolchugino town .
16	Atmospheric air Kolchugino town
17	Soil from landfill, Kolchugino town .
18	Soil from the road Yur'ev-Polskoy- Kolchugino
19	Butter from Yur'ev-Polskoy.
20	Butter from Gorochovez.
21	Butter from Suzdal.
22	Butter from Vladimir.
24	Soil from Karabanovo town.
25	Sediment from cleaning-up system in Strunino town
26	Soil from the road Suzdal-Ivanovskoye.
27	Forest soil near road Gus-Chrustalny-Vladimir
28	Soil from old industrial site in Gus-Chrustalny

Table 2
PCDDs and PCDFs in soil and sediment samples (pg/g)

Sample number	2	3	4	6	7	8	10	11	12	13	14	15	17	18	24	25	26	27	28
2,3,7,8-TCDD	<0,2	<0,2	4,7	1,2	1,3	3,9	<0,5	0,1	0,6	1,6	2,4	15,6	1,4	<0,1	0,6	<0,5	<0,5	1,5	<0,2
1,2,3,7,8-PeCDD	<0,2	<0,2	<0,2	4,3	4,1	1,1	<0,5	<0,1	2,3	<0,1	<0,1	<0,2	<1	<0,1	<0,2	<0,5	1,4	<0,2	<0,2
1,2,3,4,7,8-HxCDD	<0,2	<0,2	<0,2	<0,5	<0,1	<0,1	<0,5	<0,1	<0,1	<0,1	<0,1	<0,2	<1	<0,2	<0,2	<0,5	<0,5	<0,2	<0,2
1,2,3,6,7,8- HxCDD	<0,2	<0,2	<0,2	<0,5	16,2	2,6	<0,5	2,3	3,6	<0,1	5,5	<0,2	2,4	<0,2	2,5	<0,5	2,7	5,8	6,3
1,2,3,7,8,9- HxCDD	<0,2	<0,2	6,1	<0,5	37,2	<0,1	<0,5	1,8	<0,1	<0,1	8,4	<0,2	1,6	<0,2	<0,2	<0,5	<0,5	<0,2	<0,2
1,2,3,4,6,7,8- HpCDD	<0,5	3,2	<0,2	<0,5	145,5	<0,1	<0,5	14,1	12,0	16,3	95,7	<0,2	83,8	<0,5	4,7	9,1	2,5	1,2	11,6
OCDD	45,1	59,2	287,1	26,3	386,9	183,4	26,5	49,8	41,5	2111,3	1347,8	163,0	165,5	16,3	93,6	167,8	44,8	15,1	35,8
2,3,7,8-TCDF	<0,2	95,3	<0,2	0,7	23,1	4,0	<0,5	177,0	8,9	<0,1	2,5	22,5	9,3	<0,1	0,6	<0,5	<0,5	<0,5	<0,2
1,2,3,7,8- PeCDF	<0,1	3,0	<0,2	<0,5	9,1	<0,1	<0,5	69,2	9,7	<0,1	<0,1	<0,2	12,9	<0,1	<0,2	<0,5	<0,5	1,6	<0,2
2,3,4,7,8- PeCDF	<0,2	11,0	<0,2	<0,5	42,2	0,8	<0,5	572,0	10,1	<0,1	<0,1	16,9	33,5	<0,1	<0,2	3,5	9,8	<0,2	18,2
1,2,3,4,7,8- HxCDF	<0,2	180,0	<0,2	<0,5	269,3	<0,1	<0,5	1184,4	32,0	<0,1	8,6	<0,2	113,6	<0,2	<0,2	<0,5	<0,5	<0,2	<0,2
1,2,3,6,7,8-- HxCDF	<0,2	176,6	<0,2	<0,5	85,8	<0,1	<0,5	415,1	9,4	<0,1	<0,1	8,5	46,3	<0,2	<0,2	1,6	<0,5	<0,2	<0,2
2,3,4,6,7,8-- HxCDF	<0,2	8,6	<0,2	<0,5	129,2	1,2	<0,5	391,2	12,0	<0,1	<0,1	<0,2	<1	<0,2	2,5	1,9	<0,5	5,8	<0,2
1,2,3,7,8,9-- HxCDF	<0,2	<0,5	<0,2	<0,5	90,3	<0,1	<0,5	597,0	14,5	<0,1	20,3	136,2	5,2	<0,2	<0,2	2,5	<0,5	<0,2	<0,2
1,2,3,4,6,7,8-- HpCDF	<0,5	86,7	<0,2	<0,5	160,8	8,3	<0,5	<0,5	37,6	<0,2	21,5	55,6	268,2	<0,5	5,8	14,7	<0,5	2,5	32,1
1,2,3,4,7,8,9-- HpCDF	<0,5	<0,5	<0,2	<0,5	10,6	<0,2	<0,5	391,3	<0,2	<0,2	<0,2	<0,5	6,1	<0,5	<0,5	10,2	<0,5	<0,5	<0,5
OCDF	<1	9,2	<0,5	<0,5	53,0	33,7	<0,5	65,9	<0,5	<0,5	74,7	259,4	74,1	<1	44,9	44,8	8,9	0,7	<0,5
TEQ	0,05	52,67	5,60	3,45	93,62	5,93	0,026	570,61	15,69	3,87	9,52	41,52	40,46	0,016	1,40	2,90	5,95	2,79	10,20

Table 3
PCDDs and PCDFs in milk, butter (pg/g) and air samples (pg/m^3)

Sample number	19	20	21	22	1 (on fat basis)	5	9	16
2,3,7,8-TCDD	1,3	6,4	<0,5	<0,5	<3	0,24	0,83	0,57
1,2,3,7,8-PeCDD	<0,5	<0,5	<0,5	<0,5	<3	<0,3	<0,2	<0,5
1,2,3,4,7,8-HxCDD	<0,5	<0,5	<0,5	<0,5	<3	<0,3	<0,2	<1
1,2,3,6,7,8- HxCDD	<0,5	1,4	<0,5	<0,5	69,6	<0,3	<0,2	<1
1,2,3,7,8,9- HxCDD	<0,5	<0,5	<0,5	<0,5	103,1	<0,3	<0,2	<1
1,2,3,4,6,7,8- HpCDD	<0,5	<0,5	<0,5	<0,5	<6	<0,5	<0,2	<2
OCDD	36,1	35,4	63,1	64,4	556,8	2,43	7,37	7,94
2,3,7,8-TCDF	<0,5	<0,5	<0,5	<0,5	<1,0	<0,2	0,76	<0.5
1,2,3,7,8- PeCDF	<0,5	<0,5	<0,5	<0,5	<1,0	<0,3	<0,2	<1
2,3,4,7,8- PeCDF	<0,5	<0,5	<0,5	<0,5	144,8	<0,3	<0,2	<1
1,2,3,4,7,8- HxCDF	<0,5	<0,5	<0,5	<0,5	<1,0	<0,3	<0,2	<1
1,2,3,6,7,8-- HxCDF	<0,5	<0,5	<0,5	<0,5	<1,0	<0,3	<0,2	<1
2,3,4,6,7,8-- HxCDF	<0,5	<0,5	<0,5	<0,5	<1,0	<0,3	<0,2	<1
1,2,3,7,8,9-- HxCDF	<0,5	<0,5	<0,5	<0,5	1210,1	<0,3	<0,2	<1
1,2,3,4,6,7,8-- HpCDF	<0,5	<0,5	<0,5	<0,5	<2	<0,5	<0,2	<2
1,2,3,4,7,8,9-- HpCDF	<0,5	<0,5	<0,5	<0,5	<2	<0,5	<0,2	<2
OCDF	<0,5	17,3	<0,5	<0,5	165,0	<1	<0,5	<5
TEQ	1,34	6,60	0,06	0,06	211,40	0,024	0,91	0,58

Table 4
PAH in soil samples (mcg/kg)

Sample	Phenan-trene	Antracene	Fluoran-tene	Pyrene	Benzo(a) antracen	Chrizene	Benzo(b) Fluoran-tene	Benzo(k) Fluoran-tene	Benzo(a) pyrene	Dibenzo (a,h) antracen	Benzo(a,h,i) perilrene	Indeno [1,2,3-c,d] pyrene
1	2	3	4	5	6	7	8	9	10	11	12	13
2	37.3	5.4	58.7	16.2	14.4	19.6	8.7	2.4	-	-	-	-
3	41.5	32.9	189.7	105.3	10.7	-	16.4	5.3	4.8	-	133.6	20.7
4	109.3	23.0	132.8	73.7	73.7	7.7	11.5	3.7	2.0	-	-	-
5*	56.7	2.4	6.0	2.2	1.4	2.0	2.3	0.1	-	-	-	-
6	99.5	9.2	49.3	-	-	65.0	47.0	21.9	42.5	-	73.7	12.4
7	-	3.1	25.9	23.7	-	-	16.2	4.8	15.6	-	-	-
8	205.6	13.2	355.0	47.7	-	-	23.9	12.0	23.6	-	-	-
9*	46.6	1116.4	59.0	46.3	7.4	6.3	2.5	1.1	2.9	-	7.4	4.8
10	51.4	5.4	99.0	72.9	33.9	22.9	15.2	8.6	19.3	-	-	9.5
11	188.1	12.9	700.0	43.8	-	129.9	18.8	6.9	-	-	-	-
12	134.6	20.6	335.0	197.8	96.9	81.0	80.3	38.7	75.1	-	-	52.9
13	49.7	5.7	58.1	34.0	7.7	9.6	6.8	2.4	2.5	-	-	3.5
14	-	10.3	231.8	238.6	257.8	352.2	128.8	49.2	55.4	-	290.3	101.4
15	116.0	20.3	212.9	143.1	33.3	24.1	34.2	15.7	23.2	-	144.2	55.8
17	-	39.8	1997.0	4414.9	799.7	578.5	597.7	275.5	890.8	-	2822.9	789.1
18	69.1	2.6	34.8	-	-	-	2.9	0.9	2.1	-	-	-
20	N.D.**	N.D.	N.D.	N.D.	7.0	7.5	1.30	0.35	0.072	-	-	-
21	N.D.	N.D.	N.D.	N.D.	5.6	8.9	0.46	0.52	0.189	-	-	-
22	N.D.	N.D.	N.D.	N.D.	6.0	6.3	0.40	0.26	0.070	-	-	-
24	-	28.3	268.5	202.7	125.2	102.5	42.8	37.3	75.1	-	-	-
25	-	44.8	287.2	200.1	141.4	83.6	70.6	39.9	89.4	-	-	-
1	2	3	4	5	6	7	8	9	10	11	12	13
26	44.8	2.0	18.0	10.4	-	-	6.8	0.7	1.3	-	-	-
27	5.2	10.7	100.4	-	-	-	-	-	30.8	-	-	-
28	-	-	99.2	68.9	29.6	88.0	11.1	5.0	53.4	-	1.3	56.7

*Air sample, ng/m^3
**N.D. – no determination