LEVELS OF PCDDs/PCDFs AND DIOXIN-LIKE PCBs IN MOSCOW SOILS

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Introduction

Moscow is the capital and the largest city of Russia with the population of about 10 million people. In the past, a plenty of industrial plants were present within the city boundaries, while presently many of them have reduced production volumes or have been stopped. Such former industrial territories are often used for house-building.

A more favorable financial situation in Moscow, than in the majority of Russian cities has allowed creating in Moscow a branched network of automatic stations for monitoring of various gases in the air. Since 2005, a program has been started, directed towards estimation and monitoring of pollution levels by PCDD/PCDFs, PCBs, PAHs, pesticides, oil products, and others organic contaminants in soils. In the present paper we would like to present results of its first phase related to the study of PCDD/Fs and WHO-PCBs content in Moscow soils.

Materials and Methods

Samples (10-15g) were spiked with a PCDD/Fs $^{13}C_{12}$-labeled standard mixture (Wellington Laboratories) and extracted with 150 ml acetone: toluene mixture (10:90 v:v) at 95°C in high-performance solvent extraction system[1]. For PCDD/Fs analysis extract was cleared by acid-basic multilayer, carbon and alumina columns as described previously[2]. For simultaneous determination PCDD/Fs and WHO-PCBs samples were also spiked with a 12 dioxin-like $^{13}C_{12}$-labeled PCBs (Wellington Laboratories); and the sample preparation method was modified. Mono-ortho-substituted PCB and PCB-81 were analysed in consolidated flushing fractions from carbon and alumina column after additional clean-up procedure on activated basic alumina column (4g, activated 24h at 600-650ºC). Each analytical batch contained a method blank. All solvents, sorbent and reusable glassware were tested to ensure the absence of contaminants and interference. The PCDD/Fs and PCBs analyses were performed on GC-HRMS (Hewlett Packard HP 6890 Plus, Finnigan MAT 95XP) at resolution 10000; column SGE ID-BPX5 (30 m length, 0.22 mm id, 0.25 µm film thickness); splitless mode; oven temperature, 140°C for 1 min, 14°C/min ramp to 240°C, followed by second ramp of 20°C/min to 270°C for 15 min hold; injector temperature, 280°C; constant flow of carrier gas (He) 0.8 ml/min. Congener identification was confirmed from the ratio of the base peak and a second isotope molecular ion.

Results and Discussion

Twenty-one samples collected in various functional areas of the city were analysed. Sampling points included inhabited, green and industrial zones of Moscow; and a local background sample from the neglected ground not far from the Moscow ring motorway (conditional border of Moscow). Certainly, 21 samples are not enough for a detailed study of a big city, but these data should allow making a preliminary image of the contamination scale.

The data show that the pollution levels of Moscow soils are considerably varied. Though the average pollution of industrial zones exceeds that of inhabited territories and parks, the distinction between these zones is not obvious (table 1).

Data set on 17 toxic PCDD/PCDFs congeners was treated by factor analysis method (fig. 1). Four factors had contribution more than 1 and were taken as 64, 13, 7 and 6% of total dispersion. Factor scores pair F1-F2 and F3-F4 form perpendicular lines oblique to the coordinate's axes. Therefore, the factor rotation transforms the point set on the plane of two factors into a quantity of points approximately parallel to axes. Contributions of factors in total dispersion are 54, 15, 15 and 6%. Loadings on the first factor are mainly by PCDFs, on the second factor by 2,3,7,8-TCDD and OCDD, on the third factor by HxCDDs, and on the fourth factor, practically by only 1,2,3,7,8-PeCDD.

From the general reasons, we can suggest that the common source of pollution for all kinds of samples is the emissions of motor transport. In particular, the concentration appears to be high in the parks of the city centre. In addition, it is impossible to exclude the contribution of dust and foliage burning, widely practiced until recently. Industrial emissions inevitably lead to an increase of the contamination level, but the magnitude of this increase depends on a type of manufacture. More detailed dioxin sources can be identified when more data become available.

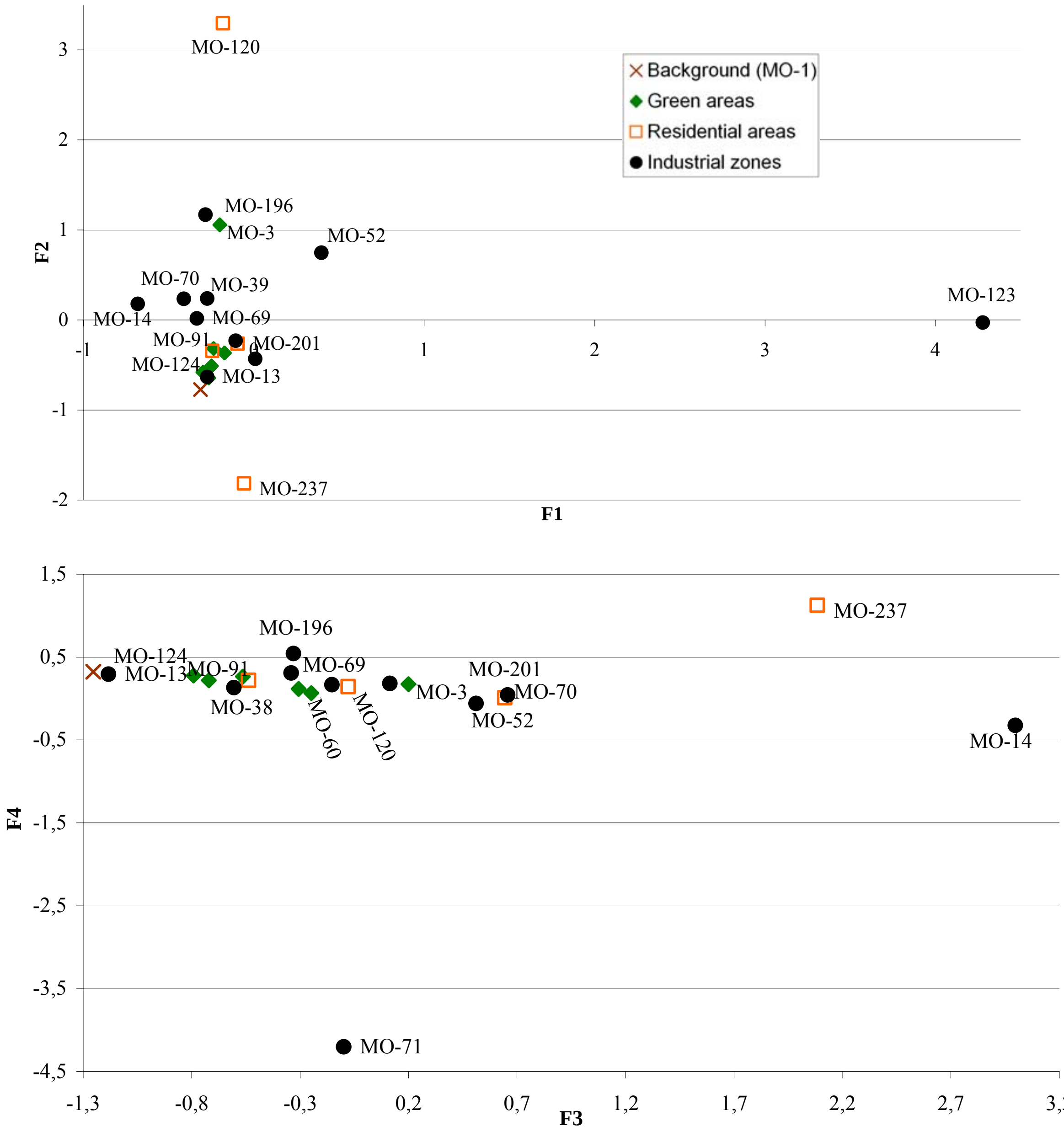

Fig. 1. Factor scores of 2,3,7,8 substituted PCDD/PCDFs.

In addition, ten samples were analyzed for the 12 dioxin-like PCBs. The observed distribution of these congeners was typical for the technical mixes, like Aroclor 1254. The WHO-TEQ of PCBs in industrial zones exceeded the $WHO\text{-}TEQ_{PCDD/PCDFs}$, while for the samples from other city areas, the contribution of dioxin-like PCBs was less but comparable with that of PCDD/PCDFs (fig. 2)

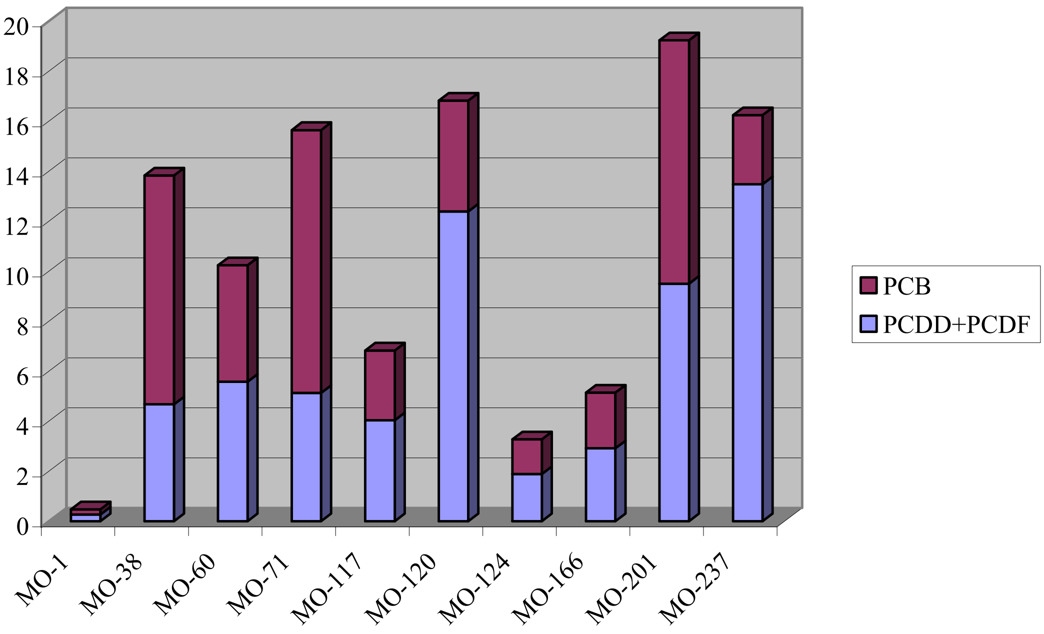

Fig. 2. Contribution of PCDD/PCDFs and dioxin-like PCB to the total WHO-TEQ, pg/g

Results of this pilot study do not allow to reveal zones of extremely high dioxin contamination. However, the dioxin pollution levels in the city soils considerably exceed the background sample values. Considering that the major part of pollutants is deposited from the atmosphere and that there is a very dust-laden air during the summer season in Moscow, the population is subject to an essential loading by dioxin-like substances.

Acknowledgements

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References

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Table 1. PCDD/PCDFs level in Moscow soils, pg/g

	Background	Green areas (n=6)			Residential areas (n=4)			Industrial zones (n=10)		
	Vacuity	min-max	average	median	min-max	average	median	min-max	average	median
2,3,7,8-D	<0,2	<d.l.-1,33	0,28	<d.l.	<0,2-1,62	0,47	0,13	<d.l.-1,78	0,55	0,45
1,2,3,7,8-D	<0,25	0,48-2,86	1,13	0,88	0,54-2,3	1,69	1,96	<d.l.-2,37	1,02	1,01
1,2,3,4,7,8-D	<0,3	0,31-0,94	0,55	0,56	0,52-1,69	1,15	1,19	<d.l.-1,96	0,95	0,81
1,2,3,6,7,8-D	<0,3	0,66-2,86	1,32	1,09	0,77-2,58	1,92	2,17	0,3-3,64	1,89	1,74
1,2,3,7,8,9-D	<0,3	0,31-1,66	0,84	0,77	0,93-1,99	1,47	1,48	<d.l.-10,8	2,21	1,19
1,2,3,4,6,7,8-D	1,00	4,63-17,59	8,23	6,52	6,64-29,3	15,7	13,5	3,22-32,2	14,9	11,9
OCDD	3,82	16,7-54,0	30,6	22,4	25,8-403	133	51,9	17,1-133	64,4	55,8
2,3,7,8-F	0,31	0,8-7,9	3,16	2,42	1,68-5,97	4,45	5,08	0,95-86,2	13,2	3,66
1,2,3,7,8-F	0,18	0,91-4,29	2,08	1,94	2,17-8,27	4,44	3,66	0,54-29,0	5,95	2,53
2,3,4,7,8-F	0,41	1,07-5,84	3,04	2,54	2,84-8,66	5,95	6,16	0,7-25,7	6,20	3,75
1,2,3,4,7,8-F	<0,25	1,66-7,84	3,74	2,95	2,94-7,72	5,75	6,17	1,38-64,8	12,3	5,66
1,2,3,6,7,8-F	<0,25	1,66-6,17	3,06	2,34	2,71-5,92	4,39	4,46	0,84-59,9	9,57	3,44
2,3,4,6,7,8-F	<0,25	0,97-4,91	2,41	2,03	2,38-4,73	3,94	4,32	0,65-30,1	6,50	3,52
1,2,3,7,8,9-F	<0,25	<d.l.-1,1	0,57	0,51	<d.l.-2,1	0,89	0,74	<d.l.-8,5	2,05	1,32
1,2,3,4,6,7,8-F	1,21	6,97-30,3	15,9	12,4	11,64-660	182	27,9	6,18-404	63,6	20,9
1,2,3,4,7,8,9-F	<0,4	0,66-1,71	1,19	1,19	0,67-3,15	2,29	2,67	0,44-44,1	6,12	1,73
OCDF	1,29	12,0-46,3	26,0	18,1	7,51-438	223	223	12,4-1690	212	45,2
I-TEQ	**0,27**	**1,68-9,83**	**4,35**	**3,43**	**3,55-13,1**	**9,26**	**10,21**	**0,91-48,66**	**10,39**	**4,95**
WHO-TEQ$_{human}$	**0,27**	**1,88-11,2**	**4,86**	**3,81**	**3,79-13,5**	**9,79**	**10,94**	**0,89-48,21**	**10,60**	**5,12**
Others TCDDs	1,24	7,09-11,5	8,47	7,32	5,38-26,0	17,1	18,6	2,54-10,7	5,63	5,59
Others PeCDDs	<0,15	7,69-48,9	26,7	22,3	15,5-32,9	26,9	29,6	4,81-26,5	15,1	14,4
Others HxCDDs	<0,3	7,23-34,3	15,8	13,8	13,1-32,3	25,2	27,6	3,93-30,5	16,7	17,6
Other HpCDD	0,85	4,66-15,7	8,14	6,89	8,91-31,4	18,5	16,9	2,91-37,9	14,1	10,1
Others TCDFs	1,02	14,3-72,6	33,9	28,1	19,7-84,2	59,9	68,1	6,32-115	33,5	24,4
Others PeCDFs	2,00	13,4-66,1	33,0	29,6	29,0-59,7	49,3	54,3	5,59-151	40,3	25,4
Others HxCDFs	1,31	4,58-37,1	16,6	14,3	14,1-286	87,0	23,9	4,64-204	39,8	17,5
Other HpCDFs	0,56	2,35-9,18	5,30	4,67	2,91-491	129	11,7	2,34-141	23,3	7,81