ORGANIC CONTAMINANTS IN THE MOSCOW REGION

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Abstract
A wide range of persistent organic pollutants (POPs) including PCDD/Fs, PCBs, chlorinated pesticides has been determined in the samples of soil, bottom sediments, waste and natural waters collected at different industrial sites of Moscow region, Russia. About half of the examined sites had moderate levels of POP pollution, while some samples of soil taken at industrial or hazardous waste sites, or samples of river sediments contained high levels of pollutants.

Introduction
Moscow region is an area of 45800 square kilometers around Moscow city. The population of Moscow region is about 7 million people. There are many settlements and industrial facilities. The data on current levels of POP pollution in Moscow region are largely absent or very scarce. This study attempted to fill this gap and provide a broad overview of levels and spatial distribution of POP pollution. This study did not include federal level enterprises, power plants and the municipal incinerators and industrial waste.

Materials and Methods
The samples were collected in October and November of 2008 at 20 industrial sites in various municipal districts of Moscow region. Were analyzed 76 individual or pooled samples, which included 53 samples of soil, 10 samples of bottom sediments, 10 samples of wastewater or natural water. The samples were collected at industrial facilities or in water bodies, which receive waste water of these facilities. At each location, several samples were taken. Some individual samples were then pooled together for further analysis. The sample collection points included municipal waste treatment plants, agro-industrial companies, transportation and construction firms, and several dumpsites.
The concentrations of PCDD/Fs, PCBs (28, 31, 52, 74, 70, 66, 81, 77, 99, 101, 110, 105, 114, 118, 123, 126, 128, 138, 153, 156, 157, 167, 169, 170, 180, 209), HCB, α,β,γ,δ-HCH, o,p'- and p,p'-DDT/DDD/DDE and other chlorinated pesticides, PAH and petroleum product were determined in most samples. All chlorinated compounds were analyzed using ^{13}C standards (CIL ES-5177-500X-0, Wellington Lab EPA-23ISS, 23RS, 23SS, WP-LCS, MBP-MPX) and HRMS technique (Finnigan MAT95XP) on SGE BPX-5 0.22x0.25x30 column for PCDD/Fs and c-PCBs; and SGE HT-8 0.25x0.25x30 column for other PCBs pesticides. Toxic equivalents (WHO-TEQ) for PCDD/Fs and PCBs were calculated with equivalency factors (1998 TEFs) recommended by the World Health Organization for human. Compound levels that were below the limit of detection limit were analyzed as zero values.

Results and Discussion
Table 1 and 2 contains the concentrations of pollutants at the most polluted sites. Persistent organic pollutants were altogether absent or present in very low concentrations in 50% of samples. For example, the samples collected at two transportation firms and a shipping company had PCDD/Fs level less than 0.2 pg/g WHO-TEQ, while other analyzed chlorinated organic compounds were practically absent. Relatively low pollution levels were typically observed near construction firms (the samples taken at Rybaki village of Ramensky district and Sychevo village of Volokolamsk district). Very disparate levels of PCDD/Fs (between 0.28 and 4.5 WHO-TEQ_{DF}) were observed in Kolychevo village of Domodedovo district, which congener pattern complicated for interpretation: PCB concentrations there varied from 0.4 to 4.6 pg/g WHO-TEQ_{PCB}, or 7.8-98.6 ng/g $PCB_{\sum 7}$(sum of PCB 28,52,101,118,138,153,180).
The pollution profiles at Vostochnaya industrial park in Cherbinka town of Podolsky district and fish processing firm "Zhemchuzhina Okeana" in Electrostal town were similar to those of waste incineration, but cumulative levels of pollution were quite modest. Maximum PCDD/Fs concentrations at these sites did not exceed 0.5 and 1.2 pg/g WHO-TEQ, correspondingly.
The samples of soil taken at municipal waste waters treatment plant in Roshal town contained moderate pollution

levels, while the sedimentation pond of this plant contained rather high concentrations of pollutants ($MR5_5$). The samples of soil taken at municipal waste treatment plant in Sofrino village (MR12) also had low levels of pollutants. While the samples of soil and water from waste waters treatment plant inlet drainage ditch taken in Istra district had elevated concentrations of 2,3,7,8-TCDD (MR3 and $MR3_{13}$).

Many companies in Moscow region are involved in waste processing, disposal or incineration. Although their activities are legal, they do not always use environmentally safe technologies. Some waste management activities lead to cross contamination of the environment by hazardous pollutants. Former industrial sites or adjacent territories are sometimes converted to illegal waste dumps, used for dumping of various hazardous substances, which creates additional risks. These territories may be also used for undisguised incineration of selected fractions of waste, dismantling of industrial equipment and bottling of oils and other technical fluids.

Our analysis uncovered very high concentrations of POPs in some parts of Salarievo industrial waste dumpsite in Leninsky district: 119 ng/g of pp'-DDT and 163 ng/g of ΣDDT/DDD/DDE, although the concentrations of dioxin-like compounds were relatively low: between 0.6 and 0.8 WHO-$TEQ_{DF/PCB}$. The samples of soil taken from reclaimed lands near Nikulskoye village of Podolsk district have shown similar levels of POPs, but the relative levels of pollutants indicated that contamination there happened earlier: 81.5 pg/g of pp'-DDT and 176 ng/g of ΣDDT/DDD/DDE. The samples of soil taken near illegal dumpsite in Mashkovo village (MR19) contained PCDD/Fs, PCBs and DDT as well as such rarely found in Russia pesticides as toxaphene (50ng/g), heptachlor (20 ng/g), aldrin (0.2 ng/g), chlordane (2.8 ng/g) and nonachlor (0.9 ng/g). Other samples contained only trace quantities of these pesticides (<< 0.1 ng/g).

High levels of pollution were discovered near Schelkovo plant of recyclable precious metals (MR20). Maximum content of PCDD/Fs in soil was 63.6 pg/g WHO-TEQ, and the concentration of dioxin-like PCBs was 28.1 pg/g WHO-TEQ. Treated wastewaters of this plant contained 61.7 pg/l of WHO-TEQ_{DF}, 12.5 pg/l of WHO-TEQ_{PCB} and 137 ng/l of $PCB_{\Sigma 7}$. The highest levels of PCDD/Fs were found in several samples of soil taken at greenhouse cropping farm “Agrofirm Podmoskovnoye” in Ostrovtsy village ($MR10_I$). The collected soil samples actually consisted of sapropel, which is mined and processed by “NPF Ecologia” company. Other samples of soil from this territory did not contain extremely high levels of pollutants. Sapropel is a generic term for sludge sediments of freshwater reservoirs. After drying, this material is used as fertilizer or food additive in cattle farming. At present, we have no information about the sources of sapropel pollution. Such large quantities of PCDD/Fs could not accumulate during drying of this material. The only feasible source of its pollution is long-term accumulation of environmental pollutants. The combination of high level of p,p'-DDD (297 ng/g) and relatively low level of p,p'-DDT (7.7 ng/g) provides an indirect proof for this hypothesis. Sapropel samples had modest concentrations of benz[a]pyren (<18 ng/g) and other PAHs. This also indicates that incineration could not be the dominant source of sapropel pollution.

Significant levels of POPs were found in the bottom sediments of the rivers which receive industrial waste waters. The sample of bottom sediments collected in Klyazma river near Sverdlovsky village of Schelkovsky district (MR18) contained the highest concentration of PCBs and DDT metabolites among all analyzed samples. This sample also had extremely high level of 2,3,7,8-TCDD. The levels of 2,3,7,8-TCDD in the samples of bottom sediments collected in Klyazma river near Schelkovo town (MR13) were 45 times lower, while the levels of other pollutants were 2 times lower. Sediments of Talitsa river (MR12) near waste waters treatment plant were polluted to somewhat lesser extent.

Therefore, the analysis of pollution at 20 industrial sites of Moscow region showed:

- *the factory where the fertilizers with high PCDD/Fs content were produced and applied;*
- *the enterprise which discharged waste water with high concentrations of PCDD/Fs and PCB;*
- *the presence of dioxin-like and other polychlorinated compounds in surface layers of soil near dumpsites;*
- *high levels of pollution of Klyazma river by dioxins, pesticides and PCBs (this river is one of the largest in the region).*

This study confirmed that overall environmental situation in Moscow region was unfavorable, and the potential for environmental proliferation of pollutants was high. These pollutants may contaminate food products and pose health risks for local population, although we have very limited data for health risk assessment.

Table 1. PCDD/Fs and c-PCBs in soil and sediment samples from Moscow area, pg/g.

	MR3	$MR3_{13}$	$MR5_5$	$MR10_I$	$MR10_{II}$	MR12	MR13	MR18	MR19	MR20
Object, n	soil, 4	sed, 1	sed, 1	soil,3	s/sed,5	sed, 2	sed, 2	sed, 1	soil, 5	soil, 2
2,3,7,8-TCDD	6,7	17	0,94	0,58	0,01	<0,04	1,4	63	1,9	8,9
1,2,3,7,8-PeCDD	0,09	0,32	0,15	21	0,10	0,20	1,1	2,6	2,0	6,1
1,2,3,4,7,8-HxCDD	0,13	0,29	0,74	30	0,05	0,19	0,7	2,0	2,9	6,4
1,2,3,6,7,8-HxCDD	0,32	0,60	1,7	73	0,09	0,49	1,3	3,3	4,0	15
1,2,3,7,8,9-HxCDD	0,32	0,47	0,72	53	0,10	0,37	1,1	1,9	3,1	10
1,2,3,4,6,7,8-HpCDD	5,6	8,4	24	635	1,6	2,7	16	58	55,3	103
OCDD	41	66	209	1090	6,4	12	332	877	399	253
2,3,7,8-TCDF	0,75	1,3	4,9	85	0,55	2,2	9,0	12	20,6	7,5
1,2,3,7,8-PeCDF	0,30	1,6	5,1	52	0,26	1,4	9,4	10	16	12
2,3,4,7,8-PeCDF	0,39	1,3	2,4	172	0,35	2,0	8,1	11	11	12
1,2,3,4,7,8-HxCDF	0,56	4,5	7,1	93	0,50	1,6	17	24	25	24
1,2,3,6,7,8-HxCDF	0,35	2,5	3,9	100	0,33	1,2	7,7	10	7,0	15
1,2,3,7,8,9-HxCDF	0,17	1,6	3,0	51	0,23	0,7	8,8	6,9	7,1	7,3
2,3,4,6,7,8-HxCDF	0,36	2,3	4,4	159	0,46	1,6	5,6	8,3	6,1	13
1,2,3,4,6,7,8-HpCDF	2,2	15	25	411	1,4	7,1	34	59	33	96
1,2,3,4,7,8,9-HpCDF	0,23	3,3	2,4	61	0,21	<0,04	10	14	7,7	13
OCDF	3,7	31	102	380	2,0	18	962	825	167	131
Total TCDD	11	23	23	1866	4	8	26	120	25	229
Total PeCDD	3	6	19	2212	4	8	23	59	41	261
Total HxCDD	5	8	23	3263	5	6	31	51	51	276
Total HpCDD	11	16	46	1442	3	5	31	106	99	197
Total TCDF	12	19	84	1574	9	38	138	158	144	143
Total PeCDF	7	22	66	1372	5	23	87	98	101	152
Total HxCDF	4	25	39	1037	4	14	73	98	90	136
Total HpCDF	6	27	39	650	2	11	79	109	62	139
PCB-77	119	208	2122	486	351	60	803	3102	801	782
PCB-81	5,3	8,6	95	34	17	2,1	22	92	38	34
PCB-126	11	15	87	72	5,2	6,0	115	511	41	84
PCB-169	3,1	1,3	3,6	24	<0,1	0,6	4,1	22	3,1	8,6
I-TEQ	**7,41**	**19,7**	**5,93**	**177**	**0,52**	**2,14**	**13,4**	**80,7**	**18,2**	**31,0**
WHO-TEQ_{DF}	**7,4**	**19,7**	**5,7**	**186**	**0,56**	**2,2**	**12,8**	**80,5**	**18,7**	**33,7**
WHO-TEQ_{PCB}	**1,47**	**2,66**	**16,8**	**8,03**	**1,56**	**0,96**	**26,6**	**76,7**	**9,26**	**15,1**
WHO-$TEQ_{D/F,PCB}$	**8,89**	**22,4**	**22,5**	**194**	**2,13**	**3,18**	**39,4**	**157**	**27,9**	**48,8**

Table 2. PCBs and pesticides in soil and sediment samples from Moscow area, ng/g.

	MR3	$MR3_{13}$	$MR5_{5}$	$MR10_{I}$	$MR10_{II}$	MR12	MR13	MR18	MR19	MR20
Object, n	soil, 4	sed, 1	sed, 1	soil,3	s/sed,5	sed, 2	sed, 2	sed, 1	soil, 5	soil, 2
PCB-28	0,55	0,81	16,7	4,6	5,6	1,3	4,8	10,7	12,9	0,85
PCB-52	1,9	1,8	14,5	1,3	2,6	4,5	14,9	33,6	13,5	8,6
PCB-66	1,2	1,3	9,0	1,9	3,1	1,6	11,0	15,7	9,0	7,3
PCB-70	1,5	1,8	12,4	1,4	3,2	2,7	14,1	27,2	10,6	12,0
PCB-74	0,80	0,66	5,6	0,56	1,7	1,2	7,1	10,4	5,8	4,5
PCB-99	1,4	5,6	12,1	1,4	1,5	2,8	38,5	46,7	13,6	17,8
PCB-101	1,6	7,6	17,6	2,1	2,1	4,1	49,3	95,5	20,0	22,0
PCB-105	0,53	1,4	15,9	0,90	2,0	0,64	25,4	41,6	9,5	13,9
PCB-110	2,0	17,5	19,2	4,7	3,0	4,9	69,8	167	28,1	37,1
PCB-118	1,3	5,0	36,5	2,0	4,3	2,3	62,8	110	21,8	29,3
PCB-128	0,25	3,1	3,2	0,73	0,39	0,55	16,7	24,4	3,5	6,1
PCB-138	1,4	4,2	15,3	2,7	2,0	1,3	59,2	106	18,6	23,4
PCB-153	1,4	9,5	12,3	2,3	1,5	2,1	46,3	82,5	17,1	19,0
PCB-156	0,18	0,54	3,6	0,31	0,49	0,12	7,9	12,6	2,6	2,7
PCB-157	0,09	0,17	0,97	0,11	0,15	< 0,02	2,5	3,5	0,77	0,90
PCB-167	0,08	0,27	1,4	0,14	0,19	0,06	3,4	5,3	1,1	1,3
PCB-170	0,19	5,9	1,2	0,60	0,18	0,27	4,5	17,6	2,0	1,5
PCB-180	0,41	6,3	4,2	0,69	0,37	0,44	9,2	30,4	5,1	3,4
PCB-189	0,03	0,07	< 0,1	0,03	0,02	< 0,04	0,30	0,66	0,12	0,15
Total PCBs	**27**	**161**	**369**	**63**	**70**	**54**	**694**	**1431**	**357**	**329**
HCB	0,20	0,91	3,5	1,6	0,92	2,7	1,7	3,5	23,8	3,5
α-ГХЦГ	0,51	0,29	0,4	0,15	0,05	0,39	0,35	0,57	0,41	0,04
γ-HCH	0,74	0,94	0,58	0,36	0,39	1,8	0,54	3,4	1,0	0,53
β-ГХЦГ	1,7	1,6	3,1	0,92	0,19	0,42	0,53	3,8	2,1	0,22
d-ГХЦГ	0,12	0,24	0,18	0,09	0,01	0,03	0,07	0,66	0,06	0,05
Σ αβγδ-HCHs	3,0	3,1	4,3	1,5	0,6	2,6	1,5	8,4	3,6	0,8
o,p'-DDE	0,34	1,1	4,7	0,21	0,05	0,17	1,98	20	12	0,71
p,p'-DDE	8,5	18,2	67	5,1	0,72	1,8	27	123	90	3,5
o,p'-DDD	3,4	53	69	55	2,0	1,4	61	326	37	9,0
p,p'-DDD	22	420	412	297	9,2	7,4	388	904	190	44
o,p'-DDT	1,7	4,2	7,5	0,9	3,7	0,63	2,0	3,8	65	0,1
p,p'-DDT	16	25	< 56	7,7	8,8	< 0,3	44	44	505	8,4
Σ op',pp'-DDT/D/E	52	521	559	366	24	11	524	1420	900	65

According with finding PCDD/Fs, PCB and DDT metabolites present the greatest risks. At the same time, virtually any hazardous substance may present high risks locally, near individual sites. The presence of HCB and HCHs isomers was typical for most samples, but the levels of these pollutants were not too high. Similar findings were previously reported in for soil samples taken in Moscow city,[1,2]. These samples also showed good correlation between PCB-126 and WHO-TEQ_{DF} (fig. 1), while there was no correlation with $PCB_{\Sigma 7}$. Based on these findings, we hypothesized that fuel burning and car exhaust gases were the leading sources of this type of pollution. The analysis of soils in Moscow region also showed correlation between PCB-126 and WHO-TEQ_{DF} (fig. 2), but in this case the correlation was less pronounced; and the correlation between PCB-126 and indicator congeners proved that there were other important sources of pollution.

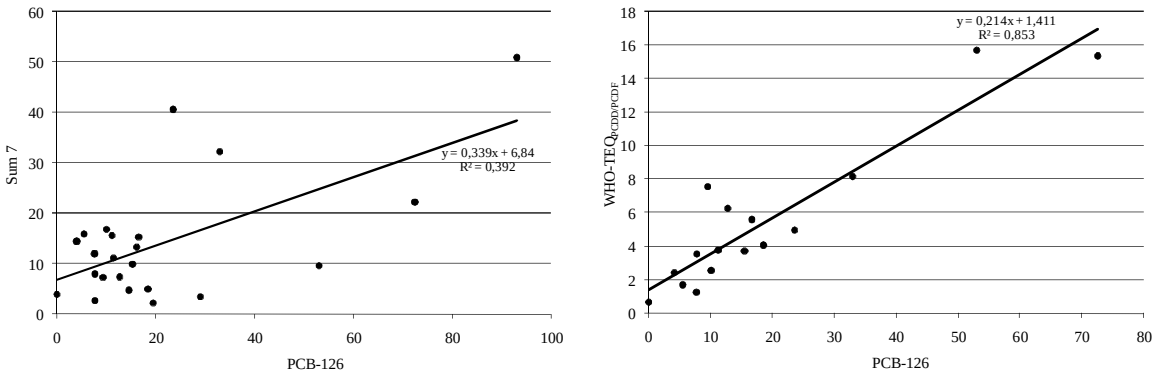

Fig. 1 Concentration of PCB-126 vs sum of seven PCB indicator congeners (28, 52, 101, 118, 138, 153, 180) and WHO-TEQ$_{PCDD/F}$ in Moscow soils (Sum7- ng/g, PCB-126 and WHO-TEQ - pg/g).

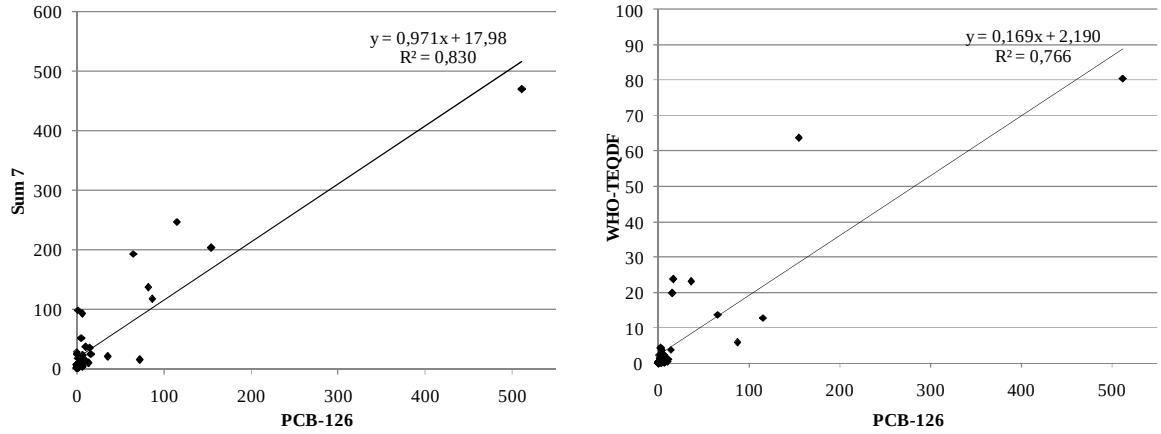

Fig. 2. Concentration of PCB-126 vs sum of seven PCB indicator congeners (28, 52, 101, 118, 138, 153, 180) and WHO-TEQ$_{PCDD/F}$ in water soil and sediment samples from Moscow area (Sum7- ng/g, PCB-126 and WHO-TEQ - pg/g).

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