ORGANIC CONTAMINANTS IN MOSCOW SOILS. LEVELS AND RISK ASSESSMENT

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Abstract
The wide range of organic pollutants, including PCDD/Fs, WHO and indicator PCBs, persistent pesticides, PAHs, oil products and others compounds, has been determined in surface soils of Moscow, Russia. In many cases, concentrations exceeded the maximum permissible values setting in Russia or European countries. The calculation system for cumulative pollution level developed to compare samples contaminated by various classes of pollutants and for assessment total environmental situation. According to the data, risk for city-dwellers almost equal from DDT/DDE/DDD and PAHs; risk from PCDD/Fs consists half from given compounds.

Introduction
Great number of industrial processes, vehicles and municipal services can result in soil pollution by different dangerous compounds. Moreover, some substances can get to the city by trans-border transfer mechanism. Since 2005, a program directed towards estimation and monitoring of pollution by PCDD/PCDFs, PCBs, PAHs, pesticides, oil products, and others organic contaminants in soils has been started. On the previous Dioxin symposium, we reported the first data for PCDD/Fs and WHO-PCBs [1]. In the given paper, we summarise all data obtained during two years researches.

Materials and Methods
Surface soils samples (0-10 cm) collected in various functional areas were analysed. From 40 up to 85 samples were studied for each pollutant group. Samples were analysed according to national certified test method. PCDD/PCDFs, PCBs and most of persistent pesticides analysis were carried out by GC-HRMS (Finnigan MAT 95XP); PAHs were analysed by HPLC-PFD; determination of oil products, phenols, some pesticides and overview analysis was done by GC-LRMS (Finnigan PolarisQ).

Results and Discussion
PCDD/F and PCBs
WHO-$TEQ_{PCDD/F}$ levels found in Moscow soils were ranging from 0.27 pg/g to 57.3 pg/g; mean concentration 8.15 pg/g for all samples and 6.9 pg/g excluding ones highly contaminated by PCBs. Proportion of PCBs in the total TEQ was highly variable, ranging from 16% to 85 %, with mean 39%, fig.1.
Concentration of non dioxin-like PCBs in most of the samples wasn't exceeded maximum allowed concentration (MAC) - 60 ng/g for PCB sum. This level approximately corresponds to Dutch target concentration - 20 ng/g for six indicator congeners (28, 52, 101, 138, 153, 180). Thus mean concentration in Moscow soils was 8.7 ng/g. Only one sample was highly polluted by PCB – 2745/4024 ng/g for six/seven indicator congeners, or 331.2 pg/g WHO-TEQ_{PCB}.
Although in general PCBs pattern is similar to wide use technical mixtures, concentration of congener #126 was poorly correlated to sum of seven indicator congeners, especially at low concentration range, while its correlation to WHO-$TEQ_{PCDD/F}$ was very good (Fig 2.) Hence, we can assume that PCB 126 and PCDD/Fs had at least one common emission source. Taking into account that pollution levels practically not connected with functional properties of territory, we can assume that source is vehicles. Though officially blended gasoline in Moscow region not is allowed, it could be delivered from other regions or produce illegally.
Chlorinated pesticides.
Concentration of DDT and its metabolites – DDT and DDD has exceeded Russian maximum allowed level (100 ng/g) in third of samples, mean concentration exceed this value at 1.5 times. Parks and recreation areas appeared to be most polluted sites of the city; domination of p,p'-DDT in profile allows us to assume that we observe contemporary pollution. Though DDT use is banned in Russia it is still may be privately included in plant protection agents or anti-mosquito chemicals and sold under other trademarks.
Hexachlorobenzene was found in most of samples at low level - <0.01- 3.3 ng/g, which is significantly lower

than Russian maximum allowed level (80 ng/g).
Levels of others pesticides from POPs list were relatively low. Heptachlor Epoxide was found in 10% of sample at level 8.9-23.1 pg/g. Chlordane and Nonachlor isomers were found in third samples at level 14.4-399.3 and 21.3-62.2 pg/g correspondingly. Mirex was detected in two of 40 samples at level below 15 pg/g, but one sample showed concentration 594.2 pg/g. This fact deserves attention, because it cannot be explained only by trans-border transfer and confirms the possibility of existence of territories polluted by "exotic" for Russia substances.
HCH was produced and used in Russia; four HCH isomers were found in most Moscow soil samples. HCH concentration varied from 0.12 to 7.54 ng/g for ΣHCH isomers and 0.05-1.54 ng/g for γ-HCH (lindane), mean value – 1.16 and 0.38 ng/g correspondently. MAC for lindane in Russia is 100 ng/g. All analised samples showed lindane concentration less than 0.1MAC. However in the same time Dutch target level for lindane 2000 time lower then Russian MAC, and in this point of view, no samples are safety [2].

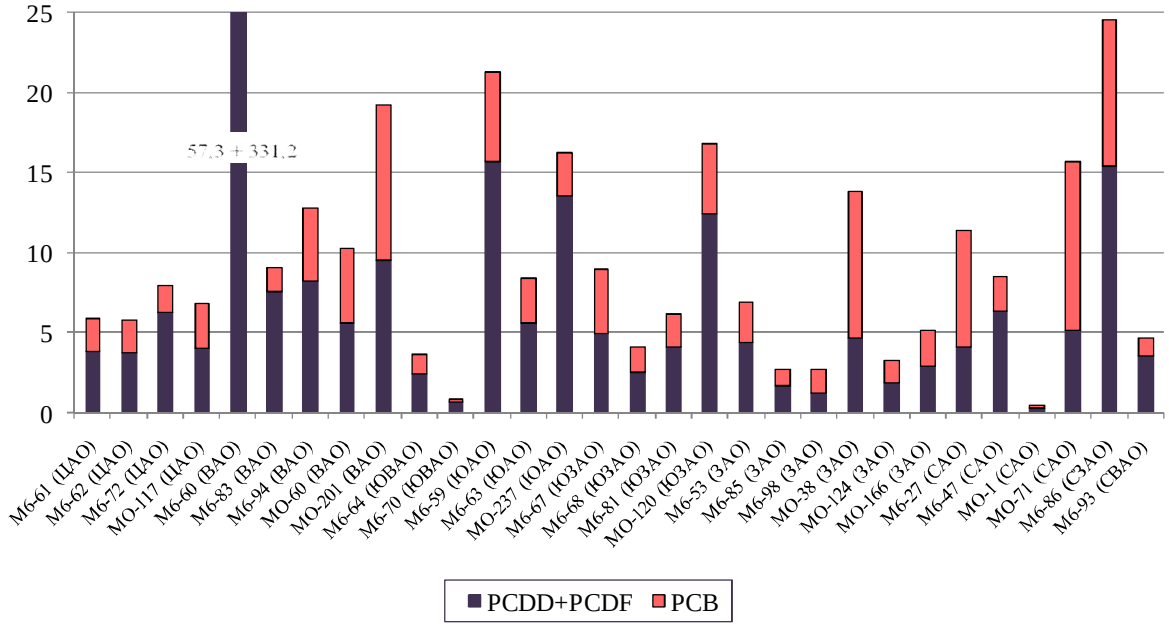

Fig. 1. Contribution of PCDD/F and WHO-PCBs to the WHO-TEQ in Moscow soils.

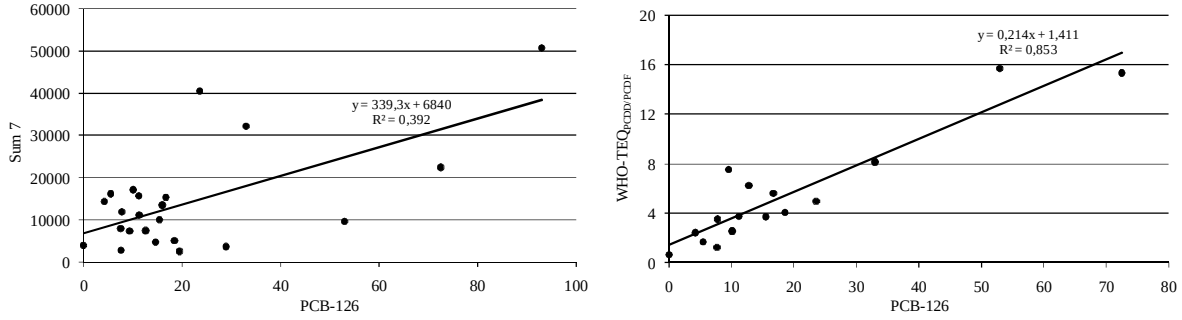

Fig. 2 Concentration of PCB-126 vs sum of seven PCB indicator congeners (28, 52, 101, 118, 138, 153, 180) and WHO-$TEQ_{PCDD/F}$.

Polycyclic aromatic hydrocarbons.
High levels of PAHs were found in most of the samples. PAH levels in 59 of 83 samples exceeded Russian MAC (20 ng/g). Moreover in 29 samples MAC level was exceeded more than 5 times; and none of the samples didn't show pollution level below 2 ng/g. Mean, median and maximal concentration for PAHs are shown on fig 3.

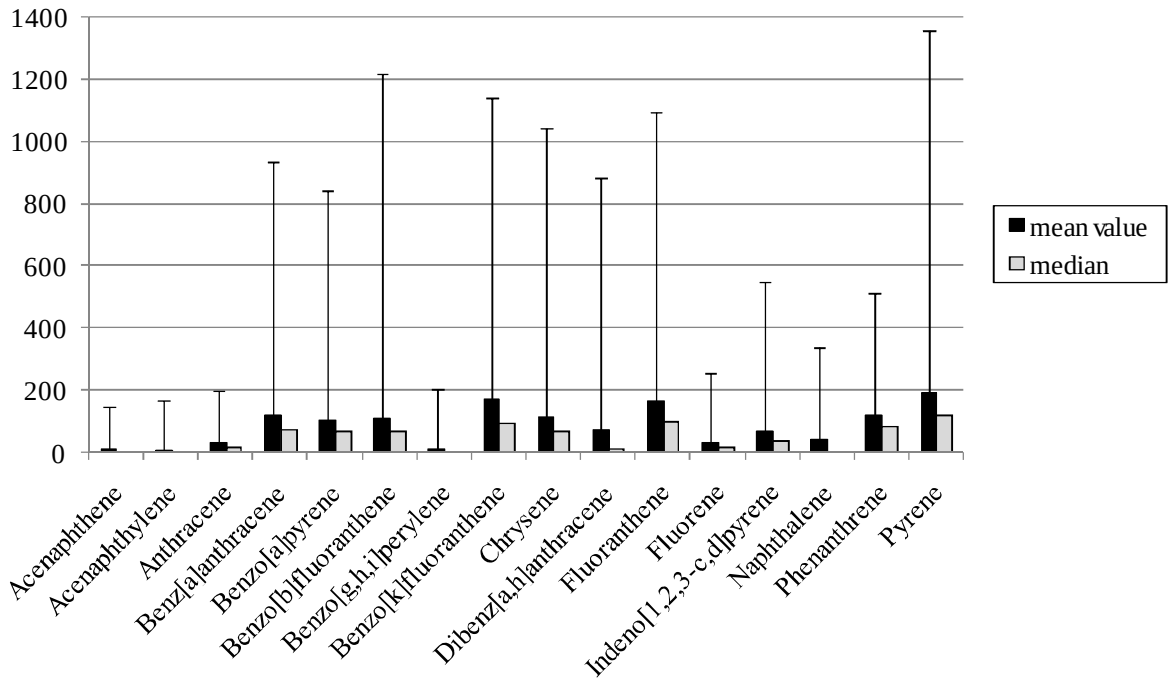

Fig. 3 Mean, median and maximal concentration of PAHs in Moscow soils (ng/g)

System of evaluation cumulative pollution level

In the urban soils there are many types of organic contaminants which can be found at elevated level. Toxicity and environmental properties of each compound could vary in wide range, and it's important to have a tool for assessment of cumulative pollution level. We offer system based on calculation of pollution index for this estimation. In the frame of short paper we want to give brief description of its underlying principles. Russian national ecological guidelines, Italian maximum allowed concentration[3] for urban and industrial soils and Dutch target and intervention values[2] were put in a basis of model; concentration range for each substance divided into 6 ranges; pollution indexes for borders of each range were assigned; pollution indexes varied as linear function of concentration within each range(table 1). If concentration of a pollutant exceeded "very high" level then pollution index was calculated by linear extrapolation of previous interval with factor 2. Any amount characteristic for the given territory groups of compounds can be use for this assessment. In given study we used seven ones. The cumulative pollution levels were calculated as the sum of individual pollution indexes, received for each group of contaminants. If group includes more than one substance, for summary used mean value, except PAHs, where averaged value for benzo[a]pyrene and mean value for others compounds.

In terms of this system acceptable cumulative pollution level could be estimated by formula 100+(n-1)*10. That is equivalent case then concentration of one component on MAC level and other components at low level. For Moscow soils mean total pollution index 3.7 times exceed acceptable level, relative contribution of each types of contaminants are shown at fig 4.

Table 1. Criteria for assessment of cumulative pollution level [*].

Group	Compounds	Pollution level (bottom value for each range				
		Low[$]	Moderated	Increased	High	Very high
1	PCDD/PCDFs, pg/g	0,1	**0,33**	5	*100*	*1000*
2	WHO-PCBs, pg/g	0,1	0,33	5	100	1000
	PCB[#], ng/g	1	5	**20**	200	*1000* [&]
3a	Benzo[a]pyrene, ng/g	1	2	**20**	500	*10000*
3b	Benz[a]anthracene, ng/g	5	100	*500*	2500	*10000*
	Benzo[b]fluoranthene, ng/g	5	100	*500*	2500	*10000*
	Benzo[k]fluoranthene, ng/g	5	100	*500*	2500	*10000*
	Benzo[g,h,i]perylene, ng/g	1	20	*100*	500	*10000*
	Dibenz[a,h]anthracene, ng/g	1	20	*100*	500	*10000*
	Indeno[1,2,3-c,d]pyrene, ng/g	1	20	*100*	500	*5000*
	Pyrene, ng/g	50	1000	*5000*	25000	*50000*
	Chrysene, ng/g	50	1000	*5000*	25000	*50000*
4	ΣDDT/DDD/DDE, ng/g	1	*10*	**100**	1000	*4000*
5	HCB, ng/g	0,4	4	**80**	200	*5000*
6	γ -HCH (Lindan), ng/g	0,01	*0,05*	*10*	**100**	500
	Σ α-, β-, γ-, и δ- HCH, ng/g	1	*10*	**100**	300	*2000*
7	Oil products, mkg/g	5	*50*	500	2500	*5000*
Pollution index		**1**	**10**	**100**	**1000**	**10000**

[*] Values of maximum permissible concentration setting in Russia are marked by bold font, standard of other counties – italics.
[$] For concentration below this value toxicity index equate to zero.
[#] Sum of six indicator congeners – 28, 52, 101, 138, 153, 180
[&] Sum of seven indicator congeners – 28, 52, 101, 118, 138, 153, 180

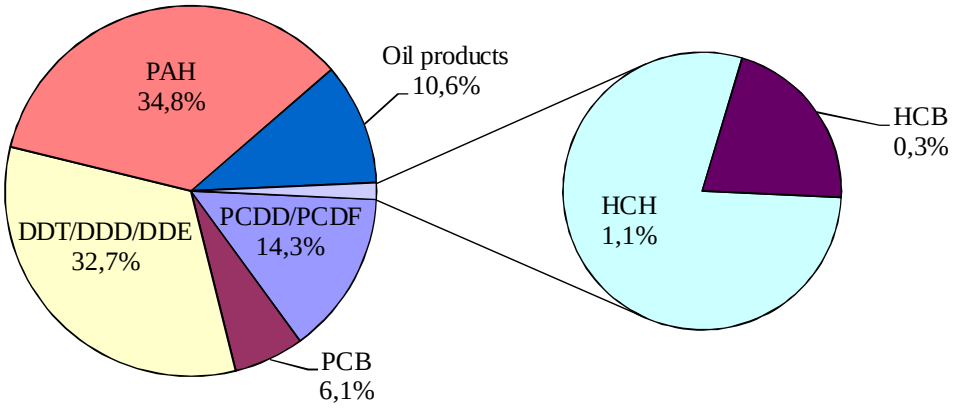

Fig 4. The contribution of each contaminant to the cumulative pollution level value in Moscow soils.

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References

1. Shelepchikov AA, Brodsky ES, Balashova SP. *Organohalogen Comp* 2006; 68: 1103.
2. Ministerie van Vollkshuivesting Ruimtelijke Ordining en Miliebeneer. Circular on target values and invention values for soil remediation. Version, februari 4th, 2000.
3. Decreto Ministerriale 25 ottobre 1999, N. 471. il Ministro dell'ambiente, Italy.