PCDD/Fs in tissues of wild animals inhabiting sites outside the landfill near Moscow, Russia

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Introduction

The environmentally acceptable management of solid domestic and industrial waste is one of the most urgent problems in Russia. For example, the total number of authorized and natural landfills in the Moscow region reaches several thousand. In addition to the visible negative impact on the environment, such landfills, serve as a source of highly toxic chemicals. The 2,3,7,8-substituted congeners of the PCDD/Fs are the most toxic. These persistent toxic compounds are ubiquitous and highly bioaccumulative in nature. Their biological activity is determined by an ability to influence cellular energy capabilities, genome activity (with shifting in genes expression and signals transduction), and carcinogenicity. The world authorities overview these chemicals and the dioxin- and POP-contaminated sites as challenges for human future generations well-being and health [1]. Accumulation of municipal solid wastes (MSW) in the open landfills near cities creates the possibility of the long-term exposure of surrounding area and humans to toxicants' (including dioxins) from some components of MSW. We investigated the ecotoxicological situation outside the sanitary zone of the landfill "Salariyevo" (Moscow) closed and remediated in 2007.

Materials and methods

The certified landfill «Salariyevo» was created near Moscow City in the early 1960s at the site of a sand pit without special devices to protect the environment from its emissions and discharges. More than 15 million tons of municipal and industrial waste were dumped and buried in the area of about 59 hectares. The landfill was shut down in 2007. Surroundings are represented by the forest park and newly built multistoried buildings. The main sampling work and animal trapping was done in 2015 and 2016 on the territory of two forested sites about 700 x 250 m each [2]. The nearest to the sanitary zone of the landfill Site 1 is located about 1 km from the dump's body. Site 2 is located about 5 km down along the river Znamenka, the forest behind the river is delimited by the buildings.

The soil samples were collected by an "envelope" method: soil aliquots were taken at a 1 m plot at its corners and in the center, to a depth of 10 cm. After aliquots mixing, 1 kg of soil was left representing one sample. Sediments samples were obtained from the nearest water bodies. At Site 1, six samples were taken from the bottom of an artificial pond; at Site 2, six samples were taken from the bottom of the old riverbed and one of the new turn of the Znamenka River.

Shrub snails (*Fruticicola fruticum*) were collected near the river, fish (*Carassius gibelio*) caught with net in the pond and small mammals trapped with standard baits [2]. There were 80 animals caught - 19 Ural field mice (*Sylvaemus uralensis*), 43 bank voles (*Clethrionomys (Myodes) glareolus*) and 18 common shrews (*Sorex araneus*). These widely represented in the European part of Eurasia species are often used for bioindication purposes.

Chemical analysis and sample preparation for chromatography-mass spectrometric analysis were done according standard method described previously [3]. Weight of abiotic samples in a dry / lyophilized form were about 10 g, animal tissues - from 7.5 to 10 g. Samples, after the addition of a mixture of isotope-labeled standards (Cambridge Isotope Laboratories), were extracted with a acetone / toluene mixture (10:90 v:v) at 95° C. The extract was purified on an acid-basic column and fractionated on activated carbon (AX-21) and basic form of aluminium oxide. A total of 10 soil samples, 13 bottom sediments, 1 fish sample, 1 snail sample and 9 mammal tissue samples were analyzed. Each mammalian sample was composed of 7-12 individuals of the same species and the whole bodies were used to prepare a sample. The samples were analyzed on a GC-HRMS Waters AutoSpec Premier. To calculate the TEQ values the Toxic Equivalent Factor model was used (WHO-TEQ_{05}) [4].

Results and discussion:
PCDD/Fs in soils and bottom sediments. The highest WHO-TEQ_{05} value in soils (10.9 pg/g) was recorded for the sample, collected earlier within the 500-meter sanitary protection zone of the landfill. Soil samples from the Sites 1 and 2 were comparable according to the WHO-TEQ_{05} levels (Site 1: average - 1.1 pg/g, median - 1.0 pg/g; Site2: average 1.3 pg/g, median 1.1 pg/g), the PCDD/Fs concentrations were almost 10 times lower than in the sanitary zone (Fig. 1). The PCDD/Fs levels in the bottom sediments' samples collected at a distance of 5 km from the landfill body (Site 2) turned out to be distinguishable among those from the old and current riverbed. In the samples from the old riverbed (without any water flow) the WHO-TEQ_{05} levels (average - 1.1 pg/g, median 1.1 pg/g) were similar to the levels in the soil samples. In a sample from a current riverbed with an active watercourse, the TEQ level was significantly lower - 0.4 pg/g. These levels were even lower in the Site 1 pond dug almost 50 years after the landfill start point – average value 0.3 pg/g, median - 0.3 pg/g (Fig. 1).

PCDD/Fs in snails and fish tissues. First animal tissues samples were obtained in 2015. The levels were registered according to WHO-TEQ_{05} - as average 1.1 pg/g for fish and 2.1 pg/g dw (10.5 pg/g lipids) for snails. TCDD average levels in these samples were 0.2 pg/g and 0.1 pg/g dw (1.3 pg/g lipids), correspondingly. Significance of these values and their influence on snails' physiological parameters was discussed by another research team [5]. The micronuclei test of fish erythrocytes showed only slight shifts of the parameters [2].
PCDD/Fs in mammalian tissues. There were variances in WHO-TEQ_{05} levels found in the tissues of small mammalian species and the contribution of PCDD/Fs individual congeners into the total toxicity level turned out to be different (Table 1). Despite the good comparability of the TEQ levels in soil samples collected at different distances from the landfill, the PCDD/Fs concentrations in the animal tissues from the Site 1 were significantly higher than from the Site 2. The levels of these substances were comparable only for the bank voles living at different distances from the dump body (1.3 and 1.6 pg WHO-TEQ_{05}/g). The excess of this toxicity characteristic was recorded for the mice and shrews from the Site 1 against the Site 2 in 2.8 and 2.1 times, respectively. This result indicates that the study and assessment of the PCDD/Fs hazard should take into account not only current levels of these substances in the habitat of organisms, but also indicators of bioaccumulation process [2]. Levels of PCDD/Fs per 1 g of lipids in the bank vole tissues from Site 1 were 1.6 times higher against Site 2. As greater accumulation of PCDD/Fs by mammals, living on the Site 1 territory against Site 2 was registered, and comparable levels of soils contamination, the toxicants absorption and falling down with water drops may be assumed. These chemicals may be transferred from the landfill by the air particles, this fact could be proved by the revealing them in tissues of shrub snails feeding on the nettle leaves.

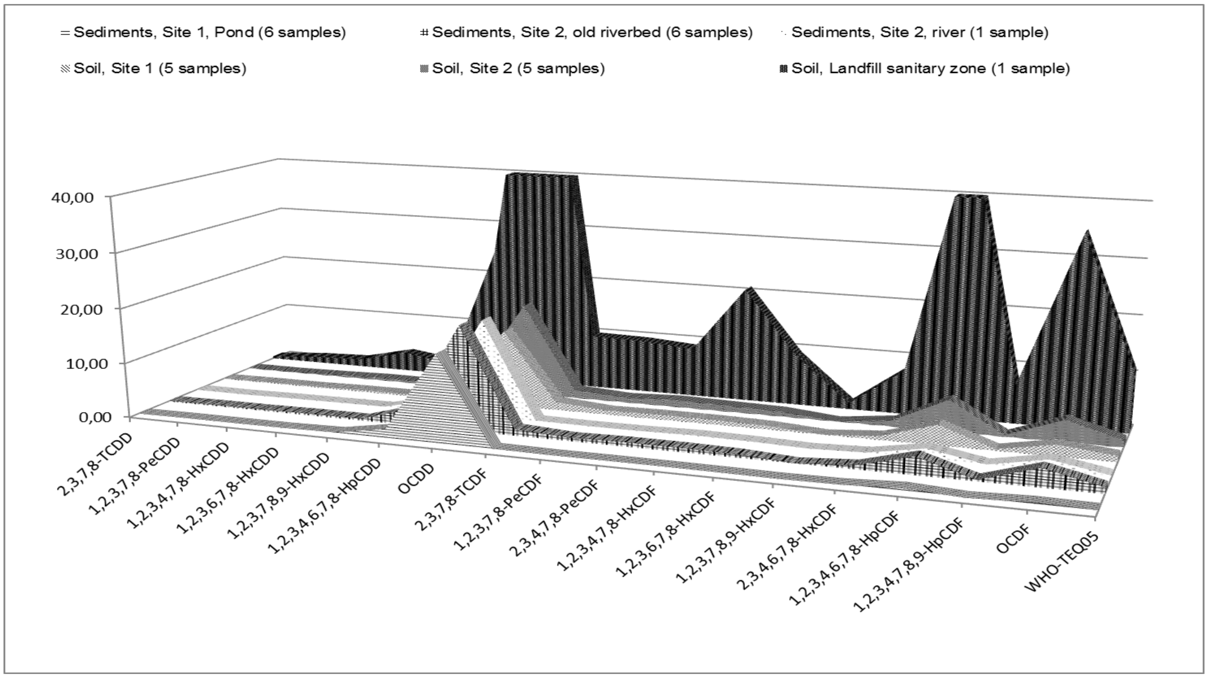

Fig. 1: PCDD/Fs (pg/g) in the soil and bottom sediments samples from the sites near the Landfill «Salariyevo»

Difference was revealed in accumulation of highly toxic congeners by these mammalian species. A significant (16-70-fold) excess of TEQ values in insectivorous shrews versus rodents may be the result of insects' prevalence in the shrew diet. At the same time, the differences between Ural field mouse (a specialized seed eating) and bank vole (a non-specialized greenery-eating) are not so definite and does not exclude the influence of their species, individual and seasonal feeding variances. The higher PCDD/Fs levels in bank voles (*Myodes glareolus*) than in short-tailed vole (*Microtus agrestis*) was registered among animals inhabiting the dioxin-contaminated areas of the sawmill [6].

<u>*Animal state specificities*</u> were manifested by PCDD/Fs accumulation in tissues of different animal species exposed to low dozes, by changes in cellular and chromosome apparatus stability, abnormalities in fish morphology and development, seasonal dynamics modification [2]. We continue to investigate these chemicals bioaccumulation effects on chronically and permanently exposed generations in nature.

Table 1: PCDD/Fs (pg/g) in animal tissues samples from the sites near the Landfill «Salariyevo»

	SITE 1						SITE 2					
	Ural field mouse (n = 12)		Bank vole (n = 34)		Shrew (n = 9)		Ural field mouse (n = 7)		Bank vole (n = 9)		Shrew (n = 9)	
	pg/g dw	pg/g lip.	pg/g dw	pg/g lip.	pg/g dw	pg/g lip.	pg/g dw	pg/g lip.	pg/g dw	pg/g lip.	pg/g dw	pg/g lip.
2,3,7,8-TCDD	0.1	0.49	0.22	1	0.31	1.7	0.05	0.18	0.15	0.46	0.21	0.89
1,2,3,7,8-PeCDD	0.26	1.3	0.45	2.4	1.1	5.9	0.04	0.15	0.43	1.3	0.91	3.9
1,2,3,4,7,8-HxCDD	0.19	0.93	0.15	0.91	0.84	4.7	0.08	0.27	0.2	0.61	0.55	2.4
1,2,3,6,7,8-HxCDD	0.25	1.2	0.25	1.5	0.85	4.7	0.05	0.18	0.36	1.1	0.55	2.4
1,2,3,7,8,9-HxCDD	0.08	0.4	0.11	0.66	0.16	0.9	0.03	0.12	0.13	0.39	0.13	0.55
1,2,3,4,6,7,8-HpCDD	0.43	2.1	0.27	1.6	1.4	7.6	0.3	1.04	0.5	1.5	1	4.5
OCDD	1	4.9	0.68	4.3	1.9	10	1.0	3.6	1.1	3.4	2	8.5
2,3,7,8-TCDF	0.19	0.91	0.47	3.1	2.3	13	0.17	0.6	0.58	1.7	1.3	5.6
1,2,3,7,8-PeCDF	0.05	0.23	0.1	0.73	0.49	2.7	0.05	0.16	0.14	0.42	0.29	1.3
2,3,4,7,8-PeCDF	3.4	17	1.3	8.5	32	177	1.1	4.0	1.7	5.2	13	55
1,2,3,4,7,8-HxCDF	1.7	8.3	0.63	4.1	5.4	30	0.68	2.4	1	3.1	2.5	11
1,2,3,6,7,8-HxCDF	1.3	6.4	0.47	3.1	7.3	41	0.62	2.2	1	3.0	3.9	17
1,2,3,7,8,9-HxCDF	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
2,3,4,6,7,8-HxCDF	3	14.5	0.54	3.5	5.2	29	1.2	4.2	1.2	3.6	2.9	12
1,2,3,4,6,7,8-HpCDF	1.1	5.4	0.33	2.2	1.8	10.3	0.89	3.1	1.2	3.6	1.4	5.9
1,2,3,4,7,8,9-HpCDF	0.19	0.9	0.08	0.51	0.38	2.1	0.06	0.2	0.24	0.73	0.28	1.2
OCDF	0.21	1.0	0.11	0.78	0.36	2	0.15	0.53	0.55	1.7	0.37	1.6
WHO-TEQ$_{05}$	**2.1**	**10.1**	**1.3**	**7.9**	**13**	**73**	**0.73**	**2.6**	**1.6**	**4.7**	**6.1**	**27**

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