PCDD/PCDFs IN SOILS AROUND OF TITANIUM-MAGNESIUM INDUSTRIAL COMPLEX

Shelepchikov AA[1], Brodsky ES[1], Feshin DB[1], Orenbah D[2].

[1]Institute of Ecology and Evolution of Russian Academy of Sciences (IPEE RAS), Leninsky pr. 33, 119071 Moscow, Russia, eco-analit@mail.ru; [2]All-Russian Society of Wildlife management, branch Berezniki.

Introduction

Manufactures of metal magnesium and titan are a potential source of environmental contamination by PCDD/PCDFs, as their technologies include chlorine, carbon and high temperature[1,2]. Though formation of dioxins in these processes is obvious, the information about environmental impact by magnesium manufactures is very limited and altogether absent for titan producing factories[3]. This study has been initiated by the public ecological organization of Berezniki city, where the titanium-magnesium industrial complex, e.g. PC "Avisma" and other industrial factories ("Soda", "Nitrogen"), is located.

Materials and Methods

Samples for the research have been collected and furnished to the laboratory for analysis by the All-Russian Society of Wildlife management, branch Berezniki.

Samples (10-15g) were spiked with a PCDD/Fs $^{13}C_{12}$-labeled standard mixture (Wellington Laboratories) and extracted with 150 ml acetone:toluene (10:90 v:v) at 95°C in a high-performance solvent extraction system[4].

The extracts were cleaned by acid-base multilayer, carbon and alumina columns as described previously[5]. Each analytical run contained a method blank. All solvents, sorbents and reusable glassware were tested to ensure the absence of contaminants and interference. 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. Congeners identification was confirmed by the ratio of the base peak and a second isotope molecular ion.

Results and Discussion

Sample point sites and PCDD/Fs WHO-TEQ levels in soils of Berezniki city are presented in fig.1 and table 1.

PCDD/Fs levels found in soils are not extremely high. But evidently two zones of soil contamination with PCDD/Fs at Berezniki city area are observed. The first one is a residential zone of the city with relatively low levels of dioxins, from 1,11 to 2,53 ng/kg WHO-TEQ (sampling points Ti 8-15). At the same time five samples from the area surrounding titan producing plant showed significantly higher PCDD/Fs WHO-TEQ levels then those in the residential area and measured up to 15,58-55,6 ng/kg WHO-TEQ (sampling points Ti 2, 3, 5-7).

Generally, congener patterns in analyzed samples are similar to those presented in the most detailed paper[1] to our knowledge. But, unfortunately, full data for all 2,3,7,8- substituted PCDD/PCDF congeners were not published, and these data concerned sewage; therefore it is impossible to make detailed comparison of the profiles. But in both cases PCDFs are dominated with PCDF/PCDD ratio >10; OCDF has the highest concentration from all congeners; levels of 2,3,7,8-TCDF and 1,2,3,7,8-PeCDF are increased within tetra- and pentachlorinated isomer groups; the concentration of 1,2,3,4,7,8-HxCDF is higher than 1,2,3,6,7,8-HxCDF and essentially exceeds that of the other two toxic congeners.

The data set has been processed by the principal component analysis (fig. 2). The two first principal components covered 94 and 4 % of the general dispersion, respectively. The first principal component is loaded by practically all variables. For the second principal component, the greatest loads gave PeCDFs, HxCDFs, TCDFs and PeCDFs. A significant part of the points falls into a compact cluster in the right top corner of the diagram; they correspond to the samples from the city. The points outside of the cluster present most contaminated samples collected nearby the industrial complex; although two points from this category are located inside the city samples cluster.

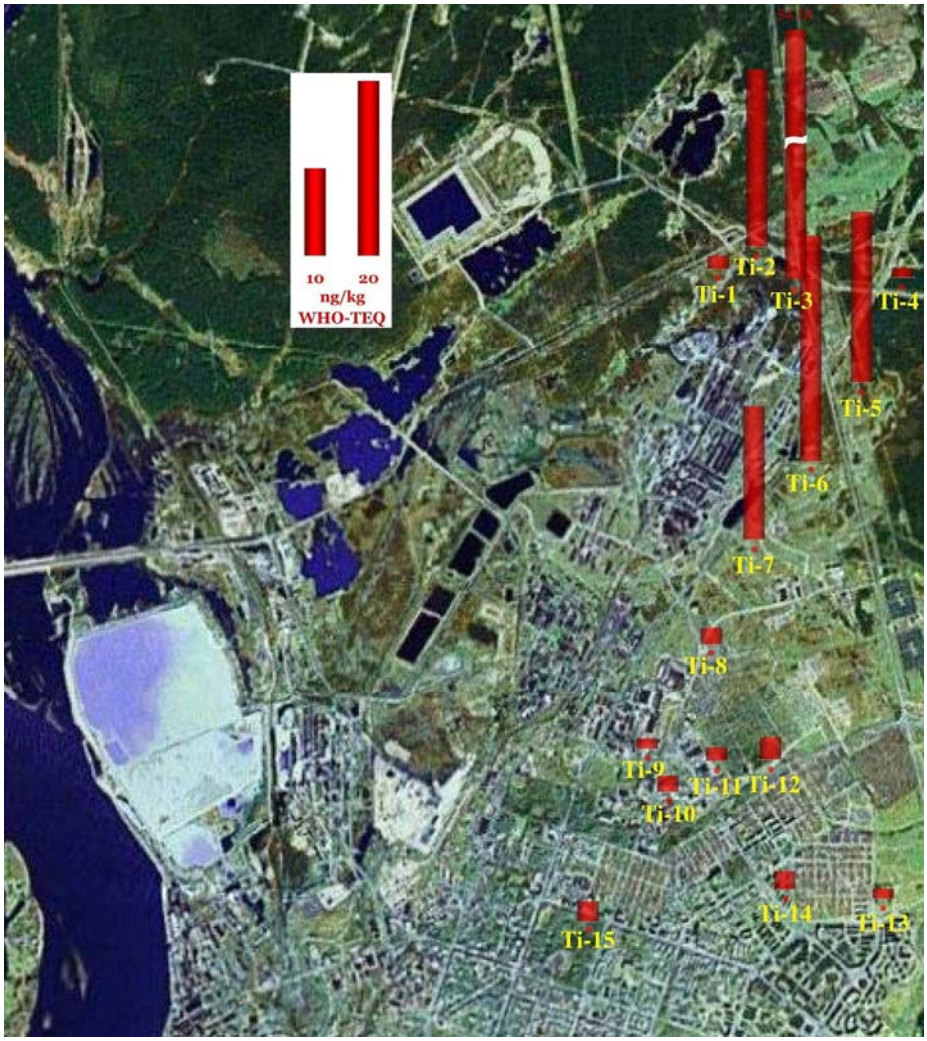

Fig. 1. Sample points and PCDD/Fs WHO-TEQ levels in soils of Berezniki city.

The congeners profile of the points within the cluster can be characterized if we exclude the data set points with the greatest differences (2,3,5,6,7) (fig 3.). Here two principal components also take up 89 and 10 % of general dispersion, respectively. Loadings on the second principal component are related to TCDD and PeCDD, and on the first principal component - with all others. In the right corner it is possible to distinguish two close clusters while other points lie separately. It is necessary to note that the points most distant from the general set along with the first principal component axis were collected near the industrial area. At the same time, samples Ti-1 and Ti-4, also collected near the industrial area, lie inside the general clusters, i.e. there is no difference in the congener profile from the city samples. Thus, it is possible to conclude that soil contamination by PCDD/PCDFs is related mainly to industrial emissions, but there also exist other sources, probably related to transportation or other urban activity.

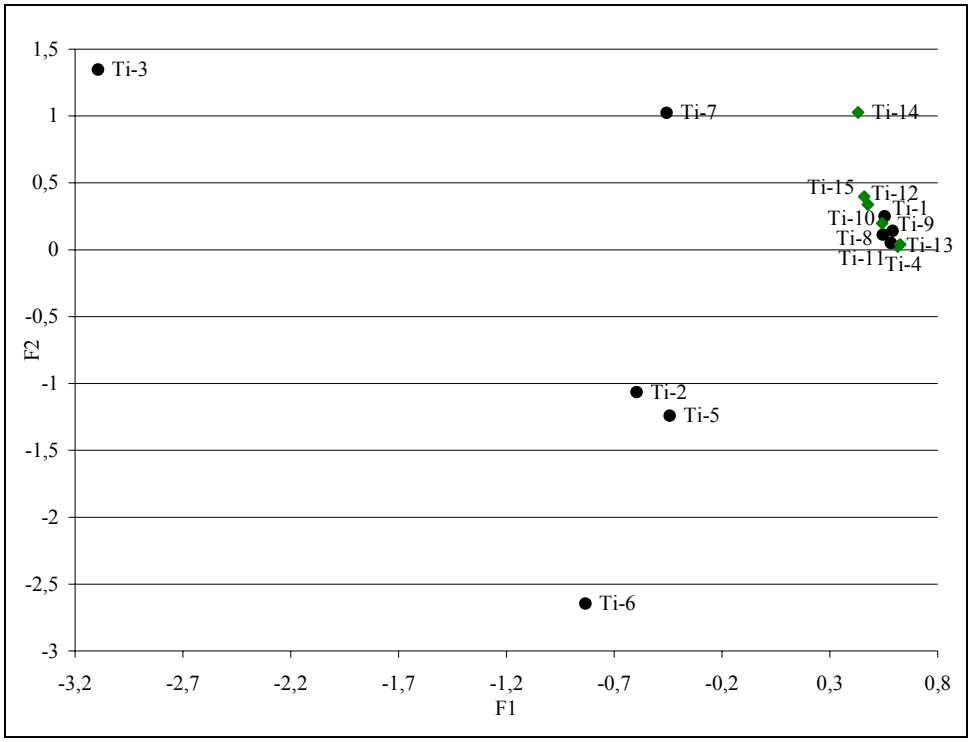

Fig. 2. Factor scores of PCDD/PCDFs for 15 soil samples from Berezniki city.

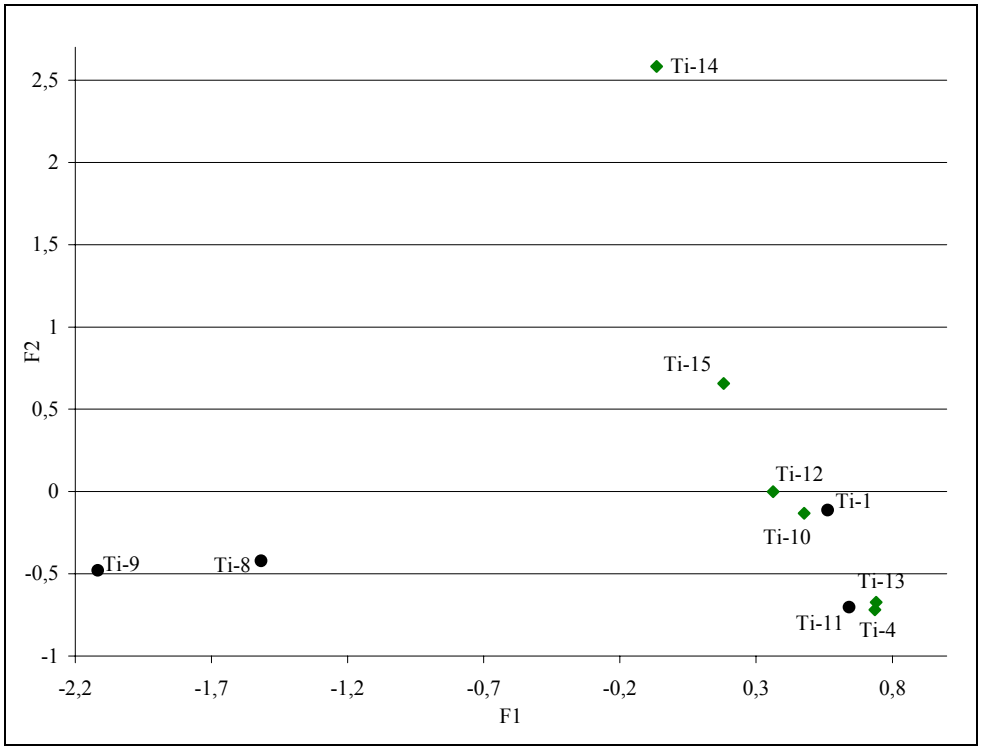

Fig. 3. Factor scores of PCDD/CPDFs for 10 less contaminated soil samples from Berezniki city.

Table 1. PCDD/F Concentrations in Berezniki city soil samples[a].

	Most contaminated samples					Others samples (n=10)		
	Ti-2	**Ti-3**	**Ti-5**	**Ti-6**	**Ti-7**	**min**	**max**	**average**
2,3,7,8-TCDD	0,87	0,95	0,10	0,28	0,25	nd	0,09	0,02
1,2,3,7,8-PeCDD	0,72	2,66	0,39	0,31	0,79	nd	0,33	0,08
1,2,3,4,7,8-HxCDD	0,71	2,82	0,52	0,67	0,88	nd	0,27	0,12
1,2,3,6,7,8-HxCDD	1,27	5,09	0,99	1,15	1,70	0,10	0,46	0,24
1,2,3,7,8,9-HxCDD	1,09	4,00	0,85	0,94	1,15	nd	0,38	0,17
1,2,3,4,6,7,8-HpCDD	9,30	38,49	9,81	9,37	11,13	0,96	2,88	1,80
OCDD	40,27	103,57	35,42	37,20	28,94	3,33	11,11	6,87
2,3,7,8-TCDF	26,91	45,29	17,73	36,89	18,50	0,59	2,36	1,57
1,2,3,7,8-PeCDF	18,82	53,02	23,03	33,06	14,48	0,69	2,12	1,43
2,3,4,7,8-PeCDF	9,97	29,36	9,98	10,14	8,60	0,57	1,50	1,04
1,2,3,4,7,8-HxCDF	36,83	104,08	43,87	55,44	24,65	2,00	4,09	2,86
1,2,3,6,7,8-HxCDF	20,53	62,68	24,73	32,80	15,25	0,96	2,74	1,77
2,3,4,6,7,8-HxCDF	11,24	29,28	11,05	16,05	8,75	0,67	1,75	1,00
1,2,3,7,8,9-HxCDF	7,75	17,66	8,39	14,92	5,25	0,34	0,97	0,55
1,2,3,4,6,7,8-HpCDF	142,50	447,09	166,74	192,30	107,71	5,37	19,69	12,36
1,2,3,4,7,8,9-HpCDF	34,19	98,22	24,42	47,32	17,79	1,07	3,86	1,88
OCDF	1812,53	2952,17	1434,99	2008,61	909,68	29,47	102,64	67,41
I-TEQ	**21,50**	**55,60**	**20,73**	**27,58**	**15,58**	**1,11**	**2,53**	**1,72**
WHO-TEQ	**20,19**	**54,18**	**19,60**	**25,90**	**15,13**	**1,05**	**2,53**	**1,69**
Others TCDD	5,68	37,99	5,83	6,78	12,18	0,88	7,08	2,45
Others PeCDD	8,14	42,98	7,13	9,74	17,61	0,68	9,49	2,63
Others HxCDD	12,60	38,69	7,96	9,12	21,03	1,03	7,84	2,89
Other HpCDD	8,94	25,60	8,41	8,45	11,40	0,78	2,75	1,60
Others TCDF	43,56	228,03	66,57	103,44	72,18	3,14	18,60	9,24
Others PeCDF	77,61	287,84	95,79	124,78	69,92	5,04	17,91	9,70
Others HxCDF	83,22	265,35	104,13	128,81	65,22	4,34	14,82	8,11
Others HpCDF	66,27	168,70	57,71	86,93	38,37	2,27	7,91	4,54

[a] Results are given in ng/kg (dry matter).TEQs were calculated based on giving values of zero for nondetects.

Acknowledgements
We would like to thank all people who organized the given research, took samples, took part in the analysis; and the INTAS project 04-82-7271.

References

1. Oehme, M.; Mano, S.; Bjerke, B. *Chemosphere* 1989; 18(7-8):1379.
2. Musdalslien, V.I.; Nokleby, P.H.; Wallevik, O. *Organohalogen Compounds* 1998; 36:81.
3. UNEP (2003) Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases *http://www.epa.ie/Licensing/IPPCLicensing/BREFDocuments/FileUpload,482,en.pdf*
4. Kluyev N., Cheleptchikov A., Brodsky E., Soyfer V. and Zhilnikov V. *Chemosphere* 2002; 46(9-10): 1293.
5. Cheleptchikov, A.A., Kluyev, N.A., Soyfer, V.S., Feshin, D.B., Brodsky, E.S. *Organohalogen Compounds* 2002; 55: 81.