SOIL SAMPLES FROM NORTH VIETNAM MOUNTAIN AS A KEY TO CLUE OCDD PHENOMENA

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Introduction

At the moment the basic industrial sources of dioxin pollution are well known, but in some cases, the analysis of environmental samples shows the significant unbalance between the amounts of PCDD/Fs entering the environment and their measured concentrations or abnormal congenerspattern[1]. Often, this abnormal pattern is characterized by predominance of octachlorodibenzo-p-dioxin (OCDD); typically, this is encountered in hot climate regions, such as Australia, Thailand[2,3], or Vietnam[4]. The true reason of this phenomenon is not known; in the literature several hypotheses are offered:

- historical contamination (volcanic explosions, forest fire, etc.);
-contamination by pentachlorophenol or others chemical;
- natural formation from natural or manmade compounds.

These hypotheses, on the one hand, prove to be true results of analyses, including received by us in Vietnam; however, on the other hand, can be denied by results for other samples and any hypothesis could not explain all cases of extraordinary OCDD contamination.

Material and methods:

The samples were analyzed by HRGC/HRMS (HP 6890 Plus / Finnigan MAT 95XP with an upgraded cooling system) using SGE BPX-5 column. PCDD/Fs were analyzed by typical procedure. Full-scan experiments were run at different scan rate and m/z interval, in order to obtain the most detail mass-spectrum. Mass measuring precision was controlled by $^{13}C_6$-PCP, D_8-DDD and native OCDD ions; in most full-scan runs, it was ± 0,02amu. We analyze organic (toluene:acetone) and basic extracts from soil samples without any clean-up or after passing through the micro column with sulfuric acid on silica gel.

Samples on five locations (in each five subsamples) of highlander area Sa Pa in north Vietnam were collected in the end of 2005. It is the hilly country with the small population which is mainly engaged in traditional agriculture. Sampling was made in hard-to-reach spots where local residents sometimes pasture cattle and are wood harvesting. In one combined soil sample concentration of OCDD reached 67 ng/g with a maximum level in one of subsamples 179 ng/g. Results of analyses and assumptions of the phenomenon reasons have been presented in Dioxin'08. Unfortunately, some conclusions have been made on not the full geographical description. Presence of predecessors in soil samples also has not been proved completely. However, relevance of these samples for decoding of the OCDD phenomenon can be even more, then we considered. Therefore, we would like to present results of the further researches.

In 2007 second expedition to Sa Pa was proven, in other points nine soil samples have been collected. The concentration of OCCD in one of them reached 0,76 ng/g and was 3-35 pg/g in others.

On the third expedition in 2010 we took personal part that had to help to better understand the specificity of studied territory. Sampling has been made in nine places, include points:

- where very high OCDD level was found previously;
- where relief is similar with most contaminated location;
- where the pollution level was low.
- sites of a congestion of rain water.

Results and discussion

Results of the analysis of some samples are presented in the table 1; facts and available assumptions below.

Fact	Supposition
The OCDD hot-spot pollution has been found at the flat top of a hill (the area ~100 м^2, height above sea level 2118 m). Surface pollution is not homogeneous, most likely original pollution was dotted. At the neighbor top (about 500 m on a straight line) high pollution is not revealed.	Less probable that in hot-spot exist the historical contamination or accumulation of pollutants deposited from the atmosphere. The source of pollution has been brought by the human
Strong forest fire was on the territory not long ago. Only trace amount of PCDFs were found. On the hot-spot hill the fragments the plastic bag identical to what are used for storage of loose goods have been found.	Forest's fire could not be a course of contamination because only PCDDs was found. Plastic bag could contain some chemicals.
We don't find any chlorinated compounds on OCDD or higher chlorination level in toluene-acetone or alkaline extracts. No one technological processes in which OCDD formed without remarkable yield of PCDFs is known. PCP (PCP salt) level in the hot-spot is higher than in other soil samples, but this level is too low to connect OCDD contamination with PCP.	PCP salt and it's water soluble impurities could be eluted by rains.
If we accept that OCDD pollution is caused by PCP, we should allow that stability of OCDD is much higher than other PCDD/Fs or OCDD could form in-situ in soil.	

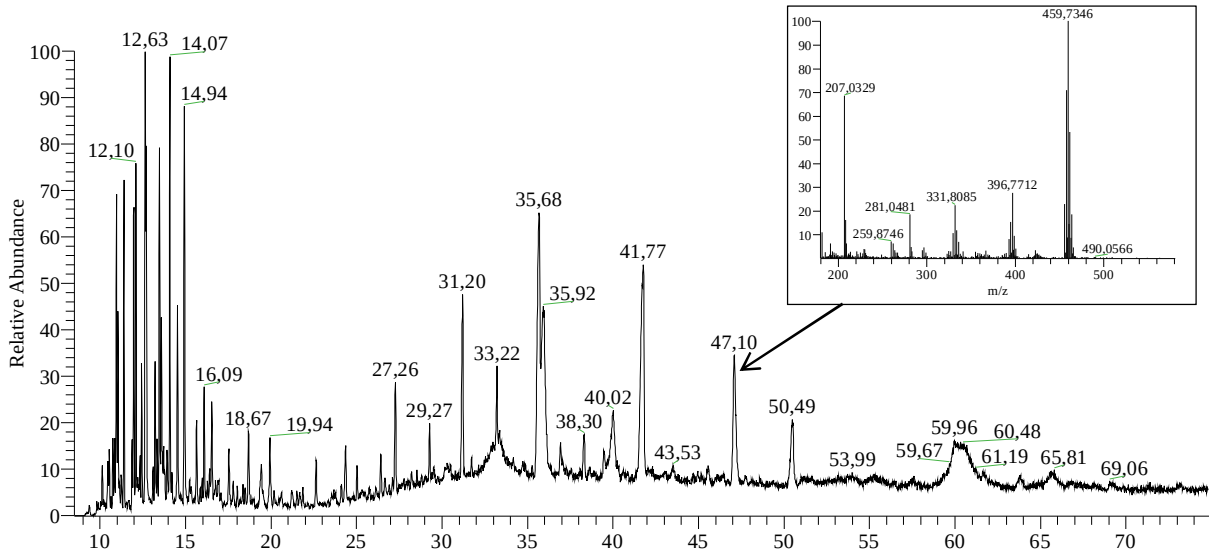


Fig. 1 TIC chromatogram and OCDD mass-spectrum of soil sample from OCDD hot-spot (m/z 180-520, 2s/d, R=8000).

In full-scan chromatograms we could recognize only two mass spectra (except PCDD), which could belong to polychlorinated organic compounds. After computer modeling possible elemental compositions for the found out ions, we recorded them in MID mode. Most abundant ions in clusters started from m/z 400 and 435 in the compound F1 are: $C_{11}H_{10}Cl_7O_3$ and $C_{11}H_{10}Cl_6O_3$. In the compound F2 - $C_{13}H_{14}Cl_8O_3$and $C_{14}H_6Cl_6O_4$,correspondingly for clusters started from m/z 448 and 498, but they could not formed from each other. These compounds were not identified, but it can be considered that they are not chlorinated polycyclic aromatic compounds.

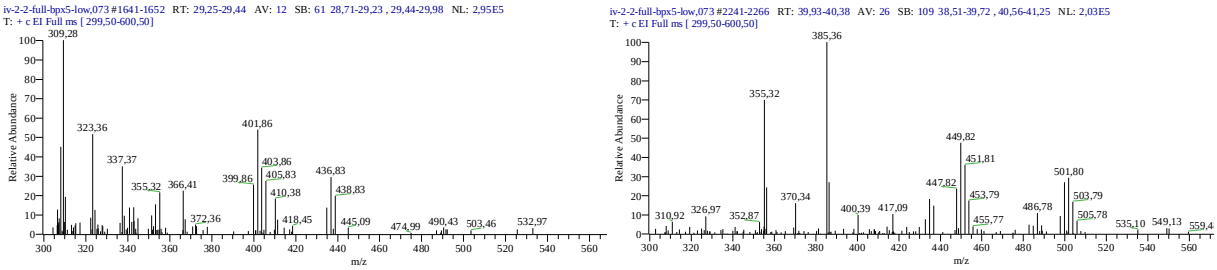


Fig.2 Substance F1(left) and F2 (right)

At a next stage, we registered ions of substances, which could be connected with the formation OCDD from PCP, including octa/nonachlorophenoxyphenol (O/NoCPhPh), decachlorobiphenylether (DeCBE), nonachloromethoxybiphenylether (NoCMeBE) and fragment ions from these and similar structures. Step by step we varied the list of registered ions in order to found elemental compositions associated with ions with highest abundances and correct isotope ration. We have not found DeCBE or O/NoCPhPh at 1:100000 OCDD detection level, but found out four other candidates (fig. 3).

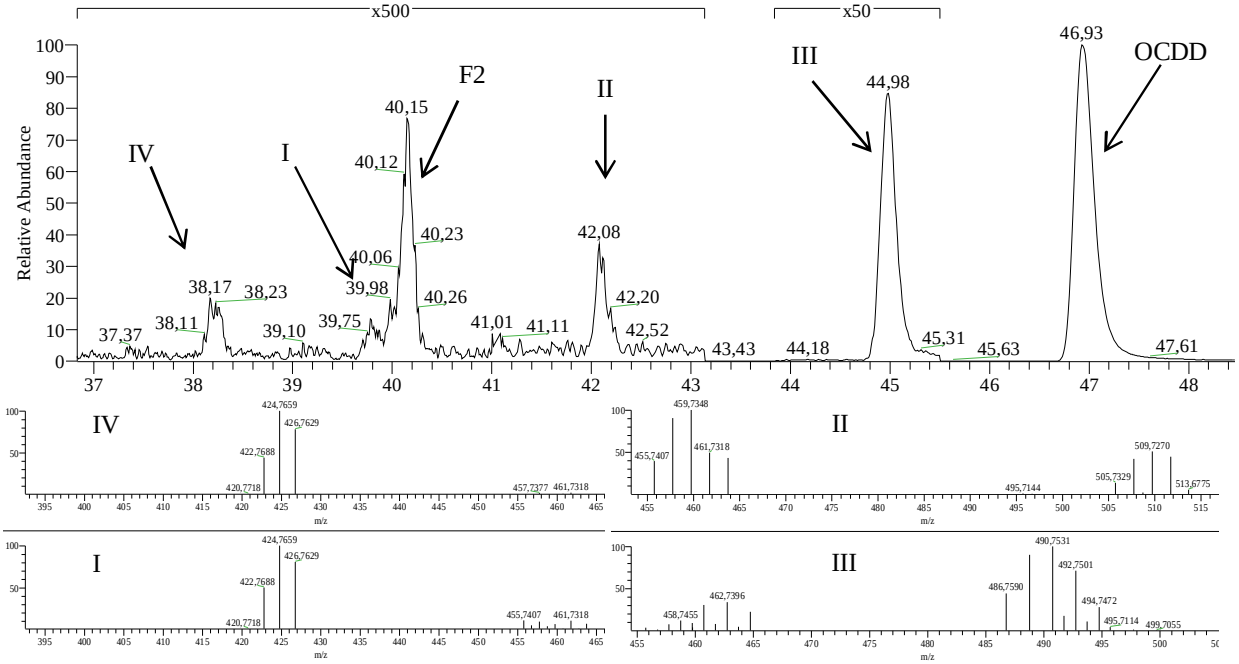
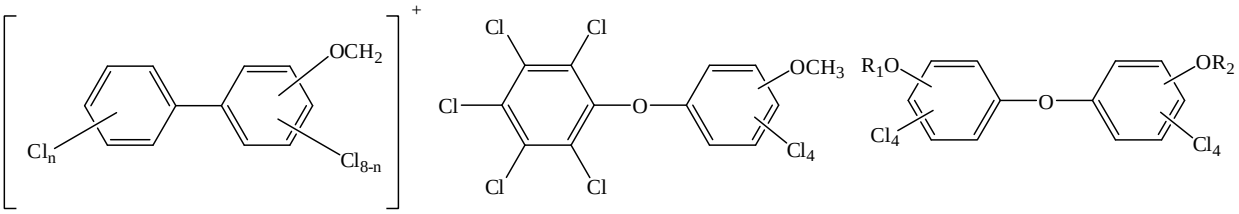


Fig. 3 MID chromatogram and mass-spectrum of possible chlorinated compounds in soil from OCDD hot-spot.

The peak of Substance I is small and strong interfered. The Substance II forms ions with m/z identical with that of OCDD and NoCMeBE. About Substance III is definitely known that it forms the ion's cluster corresponding to $[C_{13}H_3Cl_8O_3]^+$ and cluster shifted on 2 amu relative to $[C_{12}HCl_8O_2]^+$. The substance 4 forms ions shifted on 2 amu relative to $[C_{12}Cl_7O_2]^+$. Thus, now we cannot prove the structure of any discovered substances, but we can propose that:



I II III

If these assumptions are correct the found substances can be considered as a metabolite of some OCDD precursor.

Table 1. PCDD/Fs and PCP concentration in soil samples from mountain area Sa Pa in north Vietnam

	Hot-spot top (2005)					**Hot-spot top (2010)**			**Below hot spot**	**Ref. top**	**Rain water accumulator**		
2,3,7,8-D	<0,1	<0,2	<0,2	<0,4	<0,2	<0,09	<0,03	0,02	0,02	<0,02	<0,01	<0,01	<0,03
1,2,3,7,8-D	<0,2	<0,31	<0,3	3,31	<0,21	1,4	0,07	0,25	0,02	0,06	<0,01	<0,02	<0,05
1,2,3,4,7,8-D	1,1	0,84	3,3	14,2	0,47	4,2	0,17	<0,04	0,03	0,04	<0,01	<0,03	<0,03
1,2,3,6,7,8-D	1,3	1,2	3,5	20,3	0,72	7,6	0,16	1,95	0,07	0,27	<0,01	0,09	<0,05
1,2,3,7,8,9-D	6,0	1,2	6,3	21,9	1,19	12,0	0,76	2,14	0,35	0,54	<0,02	0,80	0,67
1,2,3,4,6,7,8-D	273	28,8	162	923	13,8	431	52,7	107	1,60	1,26	0,07	0,41	0,62
OCDD	**176060**	**4862**	**27940**	**136780**	**1480**	**47720**	**49090**	**13400**	**137**	**36,9**	**2,1**	**3,5**	**12,7**
2,3,7,8-F	<0,08	<0,16	<0,15	<0,3	<0,1	<0,04	<0,02	<0,02	<0,07	<0,03	<0,01	<0,01	<0,03
1,2,3,7,8-F	<0,1	<0,2	<0,19	<0,3	<0,1	<0,06	<0,04	<0,03	0,01	0,06	<0,01	<0,01	<0,03
2,3,4,7,8-F	<0,1	<0,2	<0,19	<0,3	<0,1	<0,1	<0,04	<0,03	<0,02	<0,04	<0,01	<0,02	<0,07
1,2,3,4,7,8-F	<0,1	2,2	<0,2	<0,3	<0,2	0,09	0,04	0,04	0,01	0,07	0,01	0,01	<0,02
1,2,3,6,7,8-F	<0,1	1,40	<0,2	<0,3	<0,2	0,13	0,03	<0,03	0,02	0,09	0,01	0,02	<0,05
1,2,3,7,8,9-F	<0,1	1,60	<0,2	<0,4	<0,2	0,12	<0,02	<0,03	0,01	0,27	<0,01	<0,02	<0,04
2,3,4,6,7,8-F	<0,2	0,64	<0,3	<0,4	<0,2	0,05	<0,04	<0,03	0,01	0,04	0,01	<0,02	<0,05
1,2,3,4,6,7,8-F	0,94	7,1	<0,2	<0,4	<0,2	0,76	0,37	0,21	0,14	0,38	0,13	0,06	0,13
1,2,3,4,7,8,9-F	<0,2	1,4	<0,3	<0,6	<0,2	0,04	<0,04	0,02	<0,01	0,02	0,01	<0,01	<0,03
OCDF	1,15	7,6	<0,2	<0,3	<0,1	0,48	0,27	0,21	0,07	0,23	0,08	0,06	0,09
Total TCDDs	2,7	3,2	12	7,2	3,9	1,6	0,06	0,40	0,14	0,5	<0,05	<0,09	<0,2
Total PeCDDs	<0,2	<0,3	17,7	55	2,3	17,5	0,22	5,1	0,09	0,55	<0,06	<0,02	<0,25
Total HxCDDs	93	16	85	381	9,1	161	3,9	38	1,7	2,1	0,04	2,9	1,4
Total HpCDDs	746	89	496	2619	42	1165	100	274	4,1	3,3	0,15	0,8	1,2
Total TCDFs	4,9	2,7	2,05	2,1	2,9	0,68	0,03	0,25	<0,1	1,6	<0,07	<0,1	<0,3
Total PeCDFs	<0.2	<0,2	<0.2	0,6	<0.2	0,28	<0,2	<0,3	0,13	0,46	<0,08	<0,1	<0,3
Total HxCDFs	<0.2	14	<0.2	0,6	<0.2	2,1	0,27	0,27	0,19	0,82	0,09	0,09	<0,2
Total HpCDFs	<0,3	4,3	<0,3	0,6	<0,3	1,1	0,45	0,25	0,20	0,51	0,17	0,06	0,17
PCP/PCP salt						579		NA	68	106	96	NA	94

Acknowledgements
We would like to thank all people who helped in implementation of this study, take part in sampling and analysis procedures.

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