VERTICAL MIGRATION OF PCDD/F IN VIETNAMESE SOILS.

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Introduction.

It is generally known, that during Ranch Hand operation in Vietnam (1962-1971) the US army used herbicide mixtures. These herbicide are typically contaminated with 2,3,7,8-TCDD (from 0,02 to 47ppm), thus applied chemicals consist of about 170 kg of 2,3,7,8-TCDD [1]. In current opinion, dioxins do not vertical migrate in soils (they concentrate in top 15 cm layer), given that 10 % of southern Vietnam was exposed and the half-life of 2,3,7,8-TCDD in soil about 25-100 years[2,3] the estimated level of in such place is about 50 pg/g. However in past studies we found that the concentration of 2,3,7,8-TCDD is below 1 pg/g. In a damp tropical climate such as Vietnam, the significance wind erosion is considered low; therefore, the vertical and horizontal migration of dioxins in soils was considered. In order to decision of this task was taken the samples from pits in exposure places, and also from river and marine sediments downstream from polluted places.

Materials and Methods

Location Description

Eight sampling points were selected in areas, which were identified by eyewitness or (and) kept traces of dispersion of herbicides, these sites included the village Tan Bin (province Tai Nine) and village Bien Me (province Shong Be). Sampling points included both in hill and hollow sites, that allowed the estimation of local surface migration. Samples were also collected from drainage near the former US base in Bien Hoa and in river and costal sediments from the uncontaminated province Khánh hoà.

Sampling

All soil samples were collected from pits walls, which have been dug out manually. Aqualungs in fairway collected sediments samples. For each sample about 1kg was collected.

Analysis

All samples were placed in tight plastic packing and shipped to Russian-Vietnamese tropical center in Hanoi, where samples were dried at 45-50°C and milled, then shipped to Eco-analytical laboratory of IPEE RAS, Moscow. Samples (20-25 g dw) were spiked with a PCDD $^{13}C_{12}$-labeled standard mixture and extracted with 300 ml acetone:hexane:*i*-octane: (50:45:5 v:v) at 60° C in contentious-flow extractor [4]. For these samples we applied a simplified clean-up procedure. The extracts were rotary evaporated to near dryness, dissolved in 5 ml dichloromethane (DCM) and brought to a multilayer columns, containing from top to bottom - 1 cm^3 K_2SiO_3, 1 cm^3 $MgSO_4$, 5 cm^3 40 % H_2SO_4/SiO_2, 1 cm^3 $MgSO_4$, 10 cm^3 44 % H_2SO_4/SiO_2, 1 cm^3 $MgSO_4$, 3 cm^3 K_2SiO_3 and 1 cm^3 $MgSO_4$, which were eluted with 100 ml hexane:DCM (75:25 v:v). Next the extract was evaporated to 5 ml and passed throught

pre-washed carbon micro-column (20 mg AX-21 in 180 mg Celite), column washed out with 15 ml DCM and eluted with 10 ml toluene at 100° C in back-flow. Finally the solution was rotary evaporated to 0,5-1 ml and brought to activated basic alumina column (4 g). The column was washed with 10 ml of hexane and 20 ml hexane:DCM (95:5 v:v), then eluted with 50 ml hexane:DCM mixtute (4:6 v:v). The analyses were performed on GC-MS (Hewlett Packard ÍÐ 6890 Plus, Finnigan MAT 95XL) at resolution 10000.

Results and Discussion

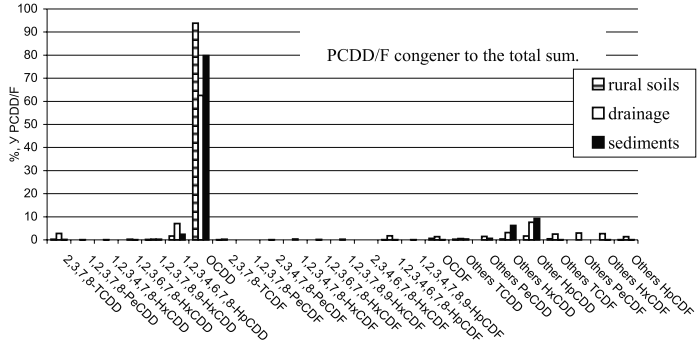
To consider the results of this study it is necessary to take into account, that tropical grounds are not capable to keep humus, i.e. to form a thick fertile layer; and that Vietnamese soils are very inhomogeneous, thus they sorbtion properties of pollutants can vary.

PCDD/Fs concentrations, pg/g dw	Drainage, run-off from fields and US airdrome Biền Hoa			Sampling point 1, Bien Me, lowland near stream			rural soils mean	Marine sediments min TEQ	max TEQ	mean	Highest blank
Depth, cm	0	20	40	5-15	50-60	80-90					
2,3,7,8-TCDD	30,94	51,7	83,05	0,48	0,11	0,06	0,70	<0,01	19,13	3,08	<0,01
1,2,3,7,8-PeCDD	2,66	2,13	2,92	<0,02	0,07	<0,02	0,00	<0,02	<0,02	0,12	<0,02
1,2,3,4,7,8-HxCDD	5,20	0,24	2,13	0,34	0,36	0,15	0,10	<0,05	<0,05	0,48	<0,05
1,2,3,6,7,8-HxCDD	10,91	1,57	4,28	0,26	0,28	0,20	0,12	<0,05	<0,05	1,41	<0,05
1,2,3,7,8,9-HxCDD	8,62	3,09	3,07	0,85	0,75	0,52	0,48	<0,05	<0,05	4,60	<0,05
1,2,3,4,6,7,8-HpCDD	187,7	131,9	100,3	7,44	2,18	1,38	4,74	9,33	40,09	36,15	<0,16
OCDD	1404	1039	1268	268,6	26,46	36,92	262,0	280,1	1142	1185	1,89
2,3,7,8-TCDF	0,96	6,37	9,15	0,18	<0,01	<0,01	0,36	0,07	0,11	0,07	<0,01
1,2,3,7,8-PeCDF	1,06	0,02	0,02	<0,02	<0,02	<0,02	0,01	0,05	0,17	0,08	<0,02
2,3,4,7,8-PeCDF	0,93	1,44	1,64	<0,02	<0,02	<0,02	0,00	0,04	0,15	0,08	<0,02
1,2,3,4,7,8-HxCDF	16,66	2,86	2,00	<0,05	<0,05	<0,05	0,03	<0,05	<0,05	0,17	<0,05
1,2,3,6,7,8-HxCDF	9,21	0,88	0,62	<0,05	<0,05	<0,05	0,01	<0,05	<0,05	0,18	<0,05
1,2,3,7,8,9-HxCDF	12,95	1,7	1,19	<0,05	<0,05	<0,05	0,01	<0,05	<0,05	0,22	<0,05
2,3,4,6,7,8-HxCDF	0,03	0,05	0,04	<0,05	<0,05	<0,05	0,02	<0,05	<0,05	0,03	<0,05
1,2,3,4,6,7,8-HpCDF	76,99	12,47	15,8	3,28	<0,10	0,30	0,38	0,46	2,94	1,14	<0,10
1,2,3,4,7,8,9-HpCDF	3,4	0,10	0,10	<0,10	<0,10	<0,10	0,00	<0,10	<0,10	<0,10	<0,10
OCDF	57,5	1,18	22,98	2,28	<0,50	1,19	1,77	1,17	2,05	2,02	<0,20
I-TEQ	**43,38**	**57,65**	**90,03**	**1,02**	**0,33**	**0,20**	**1,13**	**0,41**	**20,80**	**5,46**	**0,002**
Others TCDD	15,85	6,97	10,82	0,90	0,97	0,66	0,78	2,32	3,97	5,03	0,35
Others PeCDD	38,00	38,58	14,15	<0,02	<0,02	0,08	0,12	4,42	12,44	9,91	<0,02
Others HxCDD	98,45	41,74	45,13	1,15	0,66	0,63	1,11	39,01	130,3	93,32	<0,09
Other HpCDD	212,0	119,2	121,5	9,25	2,70	1,46	4,68	54,96	169,1	138,1	<0,1
Others TCDF	89,72	25,77	31,20	0,95	0,07	0,19	1,19	0,36	1,12	0,82	<0,01
Others PeCDF	89,31	35,25	50,61	<0,02	0,35	0,14	0,11	0,09	1,44	0,56	<0,02
Others HxCDF	92,64	29,54	36,02	<0,05	<0,05	0,20	0,11	0,26	1,18	1,12	<0,05
Others HpCDF	47,70	15,07	18,82	<0,20	0,96	0,48	0,38	<0,48	1,14	1,13	<0,20

Most of samples analysed contained 2,3,7,8-TCDD that can be unequivocally referred to the contamination of Agent Orange, as it is not known about presence of natural processes resulting in formation of this compound and in Vietnam there are no industrial sources of its considerable emission. Thus for the first time the possibility of significant dioxins vertical migration in soils was shown. Distinctions in distribution of congener groups can be explained that they entered the ground at different time, i.e. had various sources, and had various in mobility. Marine sediments are also contaminated by 2,3,7,8-TCDD, which were washed downstream by rainfall and carried out to sea.

Hence low concentration of 2,3,7,8-TCDD in surface soils can be explained by the tropical climate with high precipitation, there is an active penetration of PCDD/Fs to deeper soil layers and transport to the ocean. In contrast to the PCDD/Fs contamination in "Orange" our data showed high concentration of higher-chlorinated congeners, especially OCDD. At the present time there is no precise explanation of this phenomenon; we offer to take into account the following:

- It is known, that in Agent Orange 2,3,7,8-TCDD was dominated, but OCDD and others congener were presented in it, although the concentration considerably low. In previous studies we found that in samples from the former US base the 2,3,7,8-TCDD/OCDD ratio is 100:1 in the most polluted places (400 ng/g 2,3,7,8-TCDD) up to 1:2 in less polluted (48,2 pg/g).
- Higher-chlorinated congeners could be formed at battle actions - explosions, at use of napalm and during postwar combustion of contaminated wood and others vegetation.
- PCDD/Fs could be contained in other chemicals such as those used in agriculture, although we have no information on use of such substances in Vietnam.
- In accordance with [5], in soils the half-life of 2,3,7,8-TCDD is 103 years and OCDD is 148 years, in water 5 and 108 months respectively (at annual temperature +7C°). Therefore, since the Vietnam conflict TCDD has undergone at least 70 cycles of half destruction and only 3 cycles for OCDD. Certainly part of dioxin in a water phase cannot be significant, but exclude an opportunity of considerably faster degradation of 2,3,7,8-TCDD is incorrect.
- OCDD and other higher-chlorinated congeners may be presented in environment long before war. Recent studies by various research groups has given rise to questions of historical pollution, and although, some scientists doubt such evidence, such excellent executed works as [6] convincingly demonstrate such theory.



Acknowledgments

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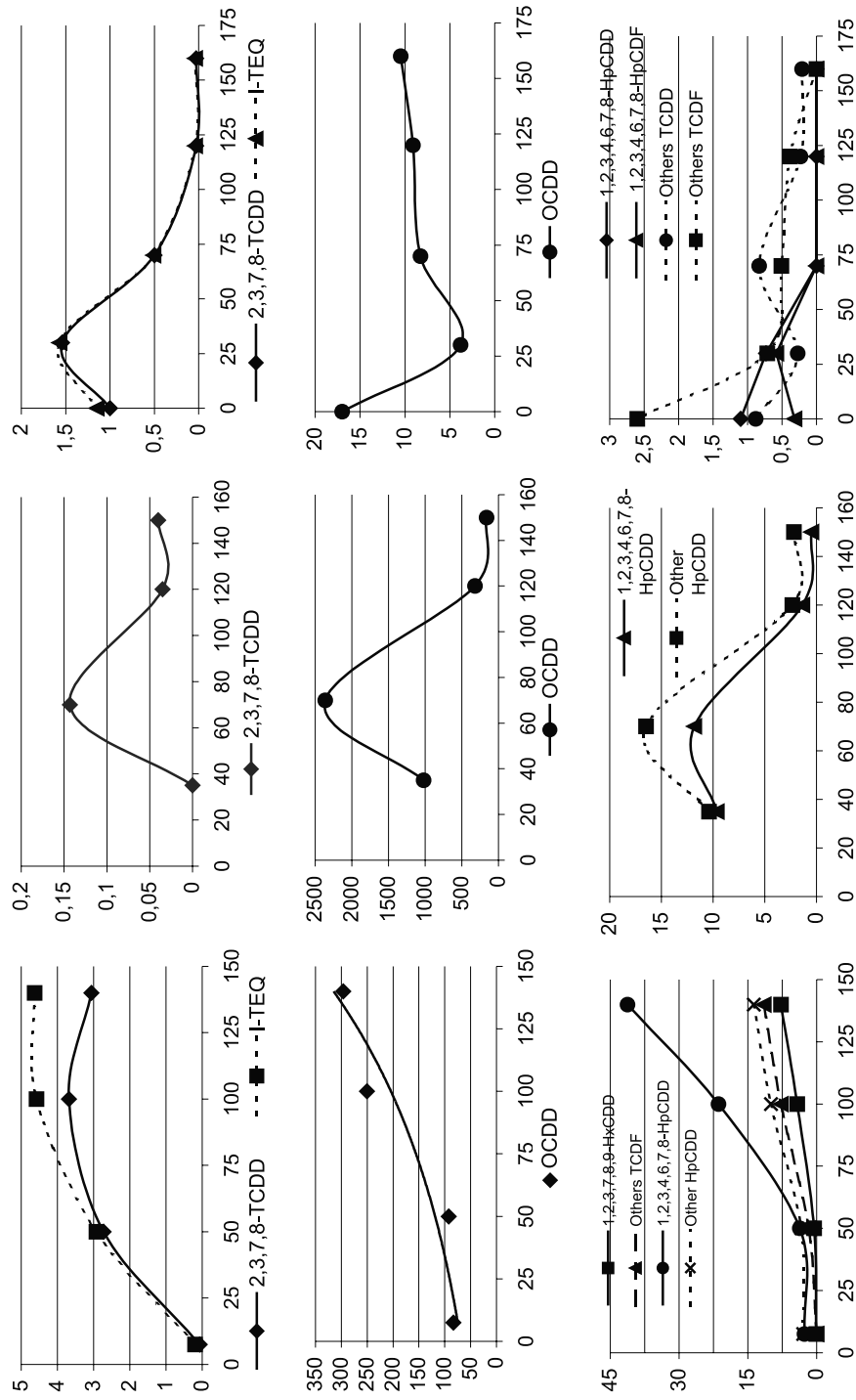

Sampling point 2, hill slope near river, village Bien Me

Sampling point 6, 150 m from road, village Tan Bin

Sampling point 8, edge of a wood near village Tan Bin

Fig.2. PCDD/Fs concentration (pg/g dw) with depth (cm).