FORMATION OF OCTACHLORODIBENZO-P-DIOXIN IN TROPICAL ECOSYSTEMS

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Introduction

A large body of factual data on the industrial sources of PCDD/Fs and their levels in the environment has now been accumulated. However, in some cases, a significant unbalance between the amounts of PCDD/Fs entering the environment and their measured concentrations or an abnormal profile of toxic congeners is observed[1]. Most often, this abnormal profile is characterized by a predominance of octachlorodibenzo-p-dioxin (OCDD); typically, this is encountered in hot climate regions, such as Australia, Thailand[2,3], or Vietnam[4]. This work presents the results of studies on detection and interpretation of abnormally high OCDD concentrations in the Vietnam ecosystem.

Material and methods:

Soil and sediment samples were taken in Vietnam in 2001-2006 by expeditions organized by the Russian-Vietnamese Tropical Center. The samples were analyzed by HRGC/HRMS at the Laboratory of Analytical Ecotoxicology of the Institute of Ecology and Evolution of the RAS.

Results and Discussion:

Usually, the dioxin contamination of Vietnam implies the consequences of the ecological disaster resulting from the use of phenoxyherbicides by the US Army in South Vietnam in 1962-1971. Altogether 72.2 million liters of herbicide mixtures was sprayed. According to different estimates, they contained 170-600 kg of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD); the contents of other 2,3,7,8-substituted congeners were much lower[5,6]. Currently 2,3,7,8-TCDD can be detected in soils and sediments in Vietnam. Except for the sites of spillage of herbicide mixtures, i.e., hot spots located at the site of some former US air bases, its concentration is very low[4]. Medium-chlorinated PCDF present in low concentrations may be indicative of the contribution of combustion processes and the overall man-made burden. However, OCDD predominates in the PCDD/F profile, while HpCDD and HxCDD are present in concentrations decreasing stepwise. The OCDD concentration in the samples, even those taken in the same area, varies over a broad range (fig 1). A general feature is a higher level of pollution of coral reef sediments compared to soils. High OCDD concentrations were also found in soil samples taken as background ones on hills in areas where no warfare took place and in the mountain massif in the north Vietnam (table 1). Typically, in the latter case, the PCDD/F concentrations in soil samples on the ridge crests and slopes are relatively low, but the soil in a valley where rainwater is accumulated contains a very high OCDD level.

Whereas the presence of 2,3,7,8-TCDD and dibenzofurans in the samples is rather obvious and readily explainable, there are no data on industrial processes resulting in selective formation of OCDD. The predominance of OCDD was noted in commercial-grade pentachlorophenol (PCP) and hexachlorobenzene, but the OCDF concentration was about 10% of the concentration of OCDD, which is seldom encountered in samples taken in human settlements and never observed in samples taken in areas remote from potential sources.

Volcanic explosions, wood combustion, and metal smelting existed well before organochlorine synthesis, which became the main source of dioxin pollution of the Earth. Analysis of archive soil samples taken in the late 19th to the early 20th century and geological deposits thousands of years old showed the presence of PCDD/F, the predominance of more stable OCDD being noted in some cases. It was suggested that dioxins formed in minor amounts during natural processes or traditional human activity could be accumulated in some geological deposits; i.e., there exists some background level that is not related to the modern technology[7,8]. However, in our opinion, this

can hardly be considered to be the main reason for the pollution of the territory of Vietnam, as this was not found for surface soils and, in addition, an abnormally high OCDD level was found only in the tropical soils, the PCDD/F profile in them being significantly different from that found in archive samples.

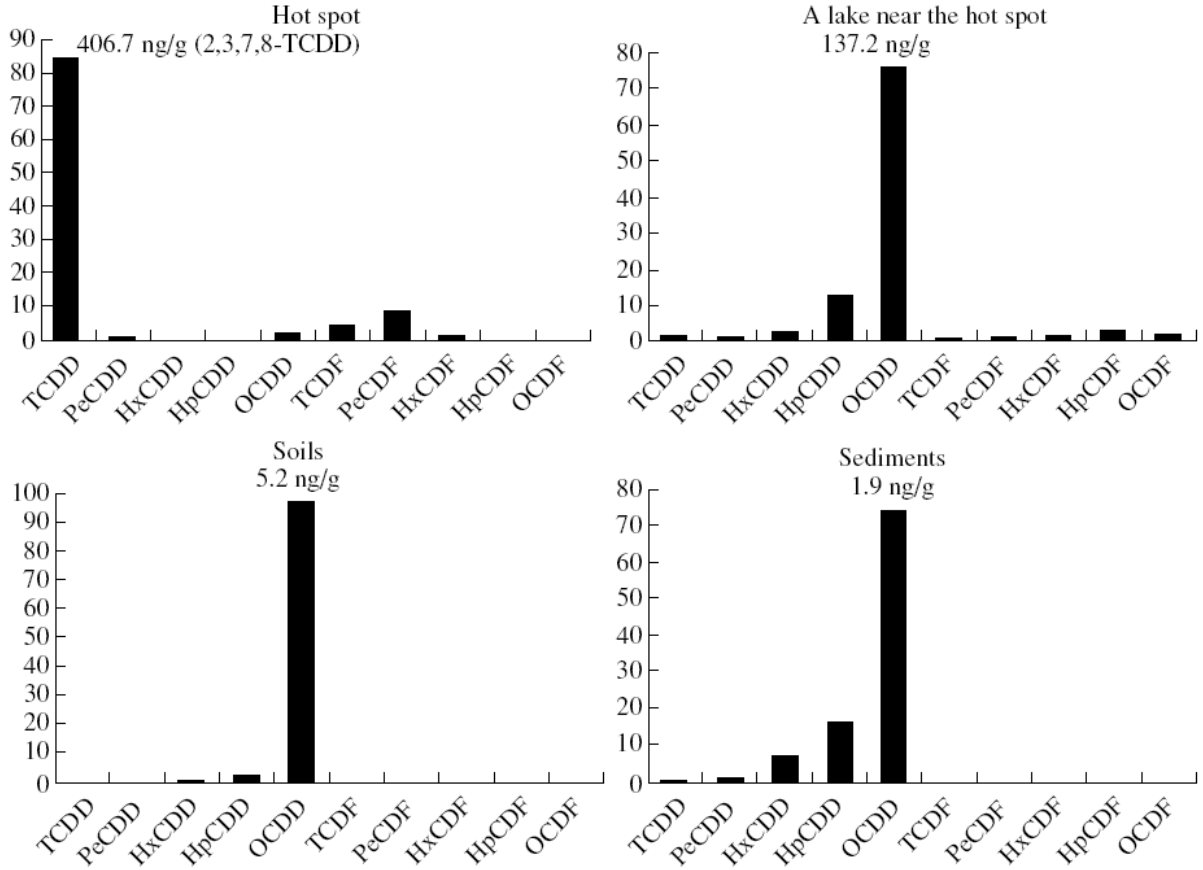


Fig. 1. PCDD/F profile in Vietnam soils and sediments (100% is the sum of concentrations of all congeners).

The pollution of areas remote from the obvious sources could result from transboundary transport, which is responsible for the highly adverse environmental situation in the polar regions. However, this is typical, first of all, of organic pollutants with medium volatilities such as PCB, DDT, or HCCH. Although highly chlorinated PCDD/F that have ended up in the atmosphere with gas discharge are subject to transboundary transport, they barely occur in the air in the molecular state but are transported with particles, which is difficult in the tropical climate. Moreover, sorbed PCDD/F are only slightly prone to photolysis, which is the only environmental process that can efficiently destroy PCDD/F, resulting in a higher relative content of OCDD.

The third cause of the pollution, which may combine several mechanisms, is the formation of OCDD from other organochlorine compounds in the environment. The most likely precursor is PCP, which has been long used for wood, fabric, and paddy-field protection. PCP is stable in the environment, soluble in water, easily sublimable, and susceptible to transboundary transport. The biochemical processes of formation of OCDD from PCP have been described; they can take place in the soil mass or sediments[9,10]. Under laboratory conditions, PCP was shown to

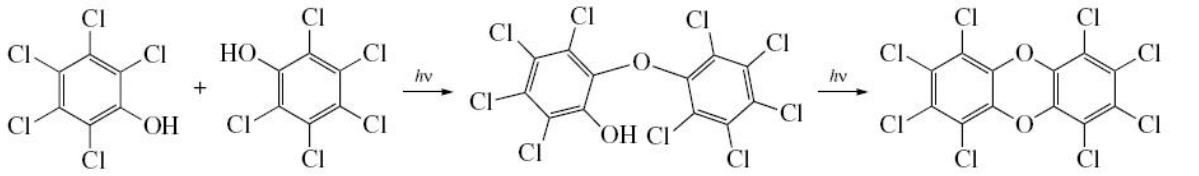
transform into OCDD on exposure to UV radiation[11]. However, the possibility of this process taking place in the environment was not proved.

The formation of OCDD from PCP should occur at least in two stages, involving 2-hydroxynonachlorobi-phenyl ether; therefore, the presence of this compound in the samples would attest in favor of this hypothesis. The detection of this compound in the environment is hampered by the fact that it is much more labile than OCDD, it is impossible to use isolation methods as efficient as for PCDD/F, and the amounts formed are very low. This concentration level is inaccessible for almost any analytical method, except GC/HRMS, which we used to determine the organochlorine pollutants in Vietnam soils. Analysis was carried out for two soil samples with high OCDD contents from mountain areas (north Vietnam and an island in the south), combined soil samples from central and south Vietnam, and two combined samples of sea bottom sediments from north and south Vietnam (table 1). A compound that can be identified as nonachlorophenoxyphenol was found only in the samples from mountain areas in concentrations proportional to the OCDD concentration (table); the content of other organochlorine pollutants in these samples was very low. No decachlorobiphenyl ether, which is an indicator of PCP use, was detected in any of the samples.

Table 1. PCDD/PCDFs concentration in Vietnam soil, pg/g

Compound	Mountain massif, north		Island
	crests and slopes	valley	peak, south
1,2,3,4,7,8-HxCDD	0.14	2.08	<d.l.
1,2,3,6,7,8-HxCDD	0.13	3.22	1.07
1,2,3,7,8,9-HxCDD	0.49	6.05	5.71
1,2,3,4,6,7,8-HpCDD	1.30	207.6	67.6
OCDD	19.3	67200	9854
1,2,3,7,8,9-HxCDF	0.19	0.21	<d.l.
1,2,3,4,6,7,8-HpCDF	0.20	0.16	0.94
OCDF	0.15	<d.l.	1.15
Others TCDD	0.51	2.9	2.66
Others HxCDD	1.26	73.4	2.91
Other HpCDD	1.34	369.2	49.6
Others TCDF	1.19	2.06	0.59
Others HxCDF	0.18	0.35	<d.l.
2-Hydroxynonachlorobiphenyl ether	<d.l.	100.1	7.3

We propose the following model that explains the formation of OCDD in tropical ecosystems and the presence of areas with abnormally high concentrations of OCDD. Pentachlorophenol, which is sublimed in the application areas, is dissolved in air moisture particles. In this state, it can be retained in the atmosphere for long periods and can be carried by atmospheric flows for long distances and undergo photochemical transformation induced by sunlight (Fig. 2).



Pentachlorophenol 2-Hydroxynonachlorobiphenyl ether Octachlorodibenzo-*p*-dioxin

Fig. 2. Scheme of formation of OCDD.

In addition, OCDD may undergo photolytic destruction to give less chlorinated PCDD with a predominance of nontoxic congeners[11]. Since the rate of photolysis increases with a decrease in the number of chlorine atoms, the concentrations of less chlorinated congeners sharply decrease. With rainwater, dioxins fall to the ground and are carried by surface waters to deposition sites. This accounts for the considerable variation of their concentrations in the soil. The high temperature, humidity, and solar activity typical of tropical latitudes are obviously favorable for the natural formation of OCDD.

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