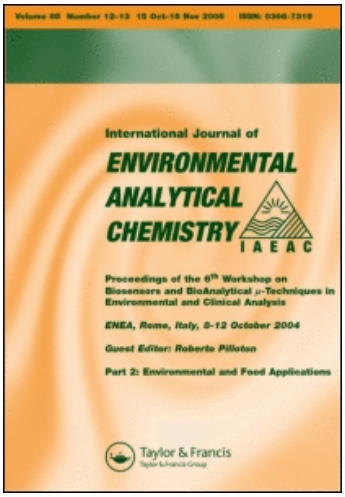

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Chlorinated Hydrocarbon Insecticide and Polychlorinated Biphenyl Residues in Soils from Southern Provinces of Vietnam

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CHLORINATED HYDROCARBON INSECTICIDE AND POLYCHLORINATED BIPHENYL RESIDUES IN SOILS FROM SOUTHERN PROVINCES OF VIETNAM

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Soil samples collected randomly from the provinces of Tayninh and Songbe, southwestern Vietnam, were analysed for the presence of DDTs, HCHs and PCBs. Residues of these chemicals were detected in all the analysed samples. Concentrations of Σ DDT in cultivated soil samples were relatively high with the highest level of 290 ng/g. However, non-cultivated soil samples recorded lower levels of Σ DDT. On the other hand, concentrations of Σ HCH were low ranging from 0.09 to 2.3 ng/g in cultivated and from 0.09 to 2.1 ng/g in non-cultivated soils, respectively. Maximum concentrations of PCBs were recorded with the highest level of 150 ng/g in a cultivated soil sample. As for non-cultivated soil samples, the highest level was found in a former U.S. air base grounds. It can then be implied that the PCBs were incorporated in the arms used by allied forces during the Second Indochina War.

KEY WORDS : DDTs, PCBs, HCHs, soils, Vietnam.

INTRODUCTION

There is a growing world-wide concern over the toxicological hazards caused by man-made chemicals to humans, animals and desirable plants. Particular attention has been paid to

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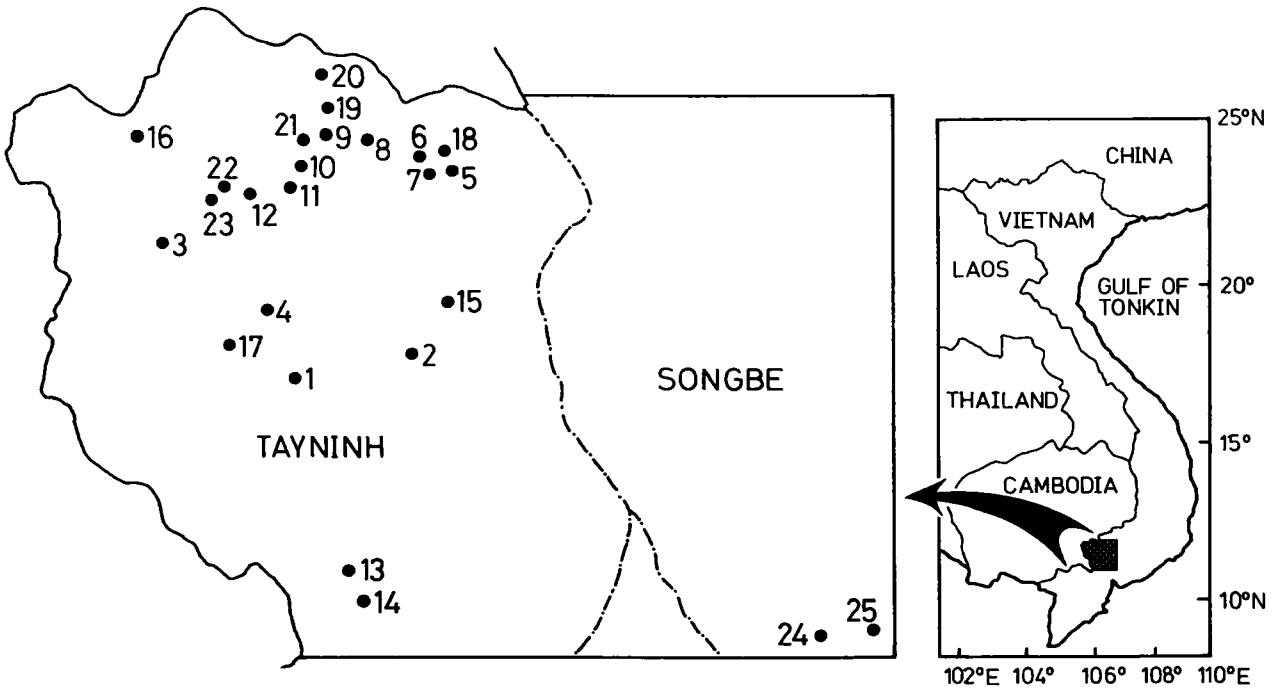


Figure 1 Map showing sampling location of soil samples from Tayninh and Songbe, Vietnam.

Table 1 Details of samples and sampling location

No.	*Nature of site*	*Sampling date*	*Sampling location*	
Cultivated Soil				
1	Paddy	23 May, 1991	Duong Minh Chau,	Tayninh
2	Green bean	23 May, 1991	Duong Minh Chau,	Tayninh
3	Paddy	24 May, 1991	Tan Bien,	Tayninh
4	Sugarcane and peanut	24 May, 1991	Hoa Thanh,	Tayninh
5	Rubber plantation	25 May, 1991	Tan Chau,	Tayninh
6	Harvested crop	25 May, 1991	Tan Chau,	Tayninh
7	Sugarcane	25 May, 1991	Tan Chau,	Tayninh
8	Harvested crop	25 May, 1991	Tan Chau,	Tayninh
9	Harvested crop	25 May, 1991	Tan Chau,	Tayninh
10	Harvested crop	25 May, 1991	Tan Chau,	Tayninh
11	Harvested crop	25 May, 1991	Tan Chau,	Tayninh
12	Paddy	25 May, 1991	Tan Bien,	Tayninh
13	Harvested crop	26 May, 1991	Go Dau,	Tayninh
14	Harvested crop	26 May, 1991	Trang Bang,	Tayninh
Non-cultivated Soil				
15	River bank	23 May, 1991	Duong Minh Chau,	Tayninh
16	Former U.S. air base grounds	24 May, 1991	Tan Bien,	Tayninh
17	Wasteland	24 May, 1991	Tan Bien,	Tayninh
18	Bombed site	25 May, 1991	Tan Chau,	Tayninh
19	School grounds	25 May, 1991	Tan Chau,	Tayninh
20	Grassland	25 May, 1991	Tan Chau,	Tayninh
21	Wasteland	25 May, 1991	Tan Chau,	Tayninh
22	Wasteland	25 May, 1991	Tan Bien,	Tayninh
23	Grassland	25 May, 1991	Tan Bien,	Tayninh
24	Around a pond	27 May, 1991	Tan Uyen,	Songbe
25	River bank	27 May, 1991	Tan Uyen,	Songbe

organochlorine compounds such as DDT and its metabolites (DDTs), HCH isomers (HCHs) and polychlorinated biphenyl congeners (PCBs). They are environmentally ubiquitous, potentially harmful, bio-accumulative and persistent[1,2]. In the 1970's, most developed nations imposed a total ban on or restricted the use of these chemicals. However, it is difficult for the developing countries, which are mostly located in the tropical belt, to stop using organochlorine insecticides since their usage is important to increase agricultural yield, protect livestock and eradicate vector borne diseases [3]. In addition, their low cost is also an economically suitable reason for them to be consumed in these countries.

On the other hand, it has been estimated that the disposal of PCBs used in old style transformers, capacitors and other electric appliances will reach its peak in the 1990's [4]. In this view, it should be remembered that developing countries might be the major holders of such goods and hence are liable to the hazards they might cause.

Vietnam, a developing Asian country of interest, is located entirely in the tropical region. Many agricultural chemicals including DDTs and HCHs are consumed in the country[5]. Besides, it was involved in a massive chemical war, which left behind many

disastrous consequences[6]. It is therefore worth studying the impact of toxic chemicals on the environment and ecosystem of the country. Our earlier studies have reported some aspects of the behaviour and fate of persistent organochlorine compounds in foodstuffs[7] and soils[8] from Vietnam. In these investigations, high values of PCBs were found in few samples collected from the remote province of Tayninh where industrial development is primitive. In the present study, besides describing DDT and HCH residues, in order to understand the source and extent of PCB contamination, a number of soil samples from Tayninh province and the adjacent area of Songbe province were collected and monitored.

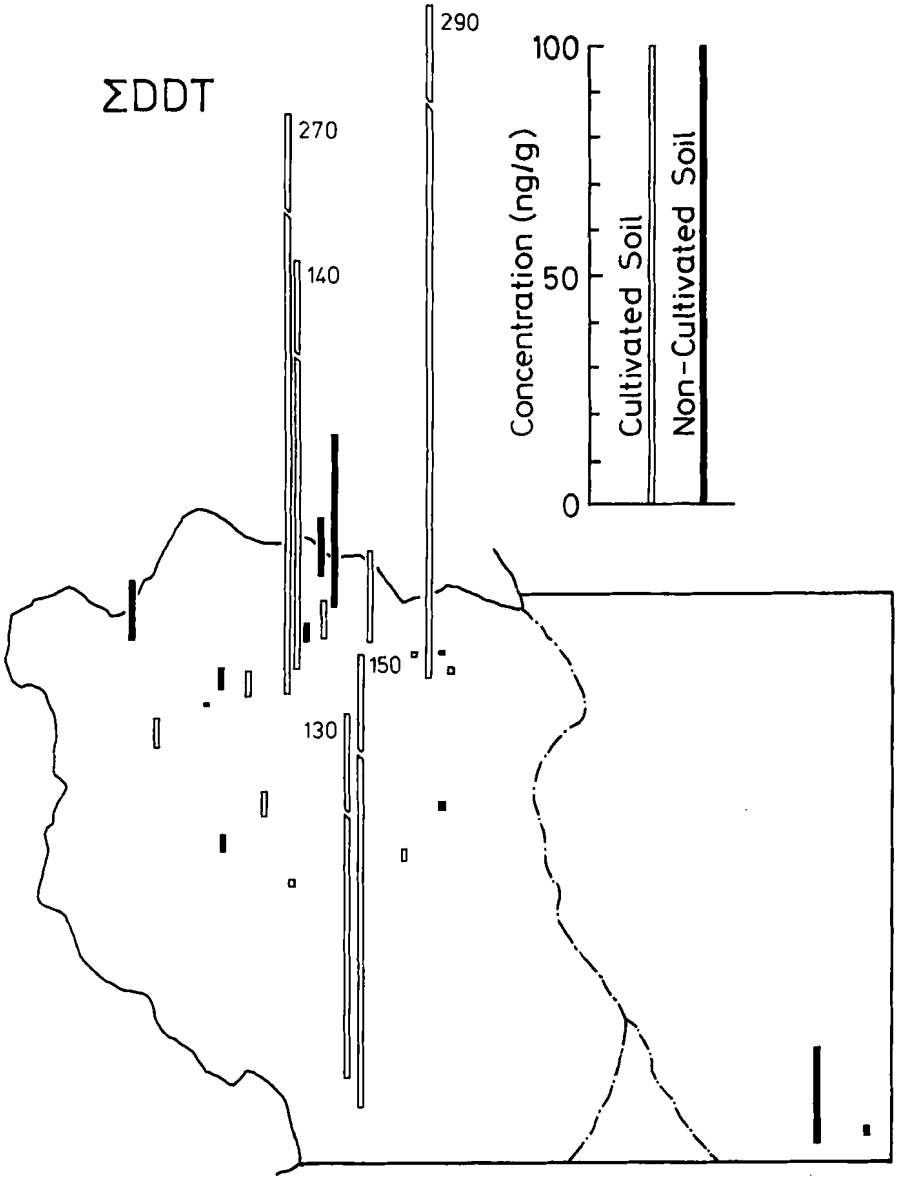
MATERIALS AND METHODS

Soil samples were collected randomly from southwestern Vietnam's provinces of Tayninh and Songbe. Details of samples and sampling locations are given in Table 1 and Figure 1, respectively. The area studied is located 150 km northwest of Ho Chi Minh city (formerly Saigon). During the Second Indochina War, the area was in "Military Zone III" according to the US army demarkation, where fierce gunfight and chemical war took place. Since it is located far from the coastal line at relatively high altitude, the area is characterized by interior-tropical climate with high temperature but low humidity. Rainfall is rather low due to large number of sunny days in a year. Along with rice, crops such as sugarcane, beans, maize and yam are extensively cultivated. Without irrigation, the soil is often dried up.

The soils were taken from 5cm surface layer into chemically cleaned polyethylene bags and transported to Japan. Organochlorine extraction, fractionation and treatments prior to analysis were done following the methods described previously[8].

Quantitative determination of the chemicals was performed on a Hewlett Packard 5890 Series II model gas chromatograph equipped with ^{63}Ni electron capture detector and moving needle-type injection system (splitless and solvent cut mode). The capillary column consisted of fused silica and chemically bonded DB-1 having dimensions 0.25 mm i.d × 30 m length and stationary phase film thickness of 0.25μm. Column temperature was programmed from 160 to 240°C at a rate of 2°C per minute. Helium was used as carrier gas and make up gas was nitrogen. Injector was kept at 250°C while detector was kept at 300°C. DDTs (*p,p'*–DDE, *p,p'*–DDD, *o,p'*–DDT and *p,p'*–DDT) and HCHs (α–, β–, γ– and δ– isomers) were quantified from individually resolved peak heights with corresponding peak heights of the standards. An equivalent mixture of Kanechlor PCB preparations (KC-300, KC-400, KC-500 and KC-600), with known PCB concentration and content as described in Tanabe et al.[9], was used as standard for the quantification of PCBs. Concentration of PCBs in the samples was calculated by adding the concentrations of individually resolved peaks of different congeners.

Recovery rates of organochlorines with spiked samples exceeded 90%. The minimum detection limit for DDTs, HCHs and PCBs were 0.005, 0.001 and 0.05 ng/g, respectively. Concentrations of the analysed organochlorines were not corrected for the recovery rates.



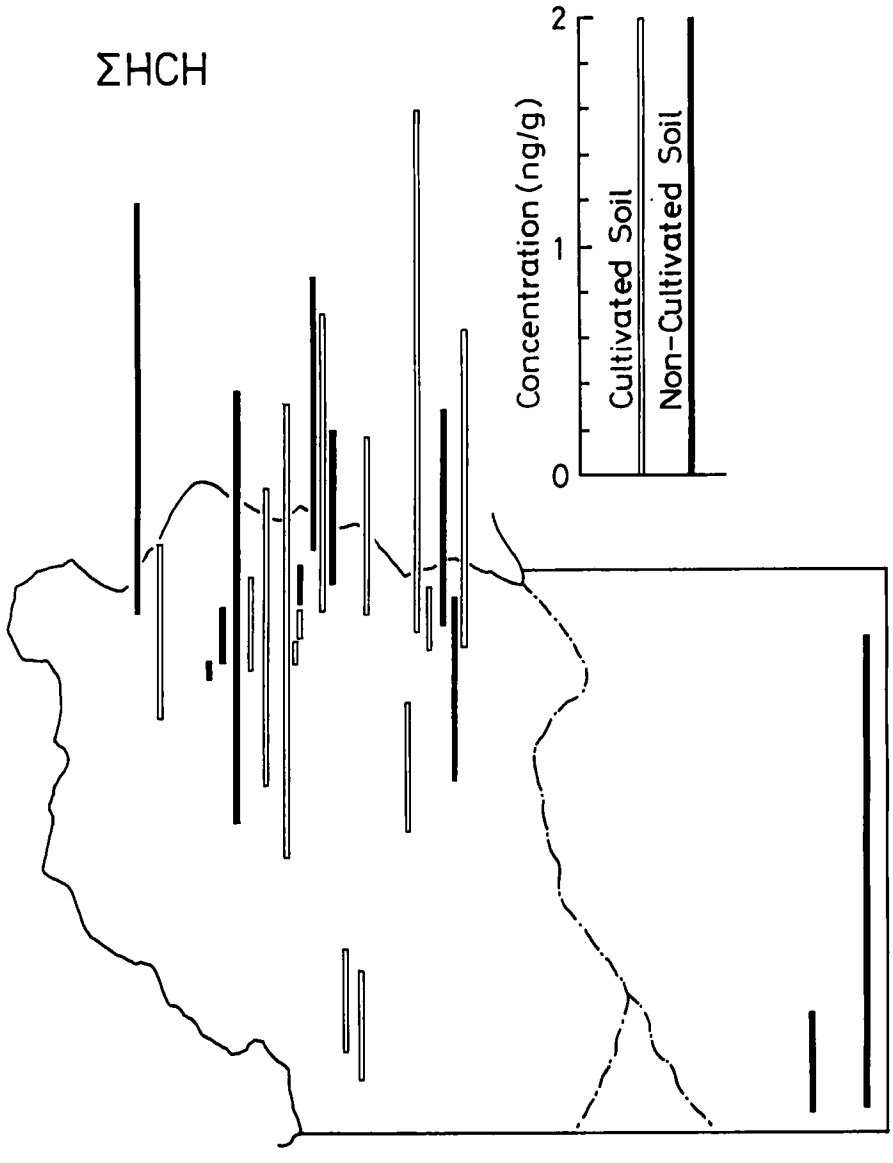


Figure 3 Spatial distribution of Σ HCH in soils from Tayninh and Songbe, Vietnam.

Table 2 Concentrations of ΣDDT, ΣHCH and PCBs in soils from Tayninh and Songbe provinces of Vietnam (ng/g, dry wt)

No.	*Σ DDT*	*Σ HCH*	*PCBs*
Cultivated			
1	1.9	2.0	2.3
2	2.4	0.57	1.8
3	6.6	0.78	2.3
4	5.1	1.3	1.6
5	1.6	1.4	1.0
6	1.0	2.3	8.7
7	290	0.27	0.45
8	20	0.78	0.95
9	8.8	1.3	2.0
10	140	0.12	9.5
11	270	0.09	150
12	5.7	0.42	1.0
13	130	0.46	32
14	150	0.47	38
Non-cultivated			
15	1.5	0.80	5.0
16	13	1.8	92
17	3.5	1.9	6.4
18	0.46	0.95	25
19	38	0.67	13
20	13	1.2	1.9
21	3.9	0.16	5.9
22	4.4	0.24	1.2
23	0.25	0.09	0.23
24	26	0.44	13
25	2.0	2.1	3.1

RESULTS AND DISCUSSION

Concentrations of ΣDDT (*p,p'*–DDE, *p,p'*–DDD, *p,p'*-DDT and *o,p'*–DDT), ΣHCH (α, β, γ and δ isomers) and PCBs in cultivated and non-cultivated soil samples are given in Table 2. Spatial distributions of ΣDDT and ΣHCH residues are shown in Figures 2 and 3. Percentage compositions of DDT and its metabolites and HCH isomers are exhibited in Figures 4 and 5. Spatial distribution of PCBs residues is shown in Figure 6.

Noticeable levels of ΣDDT, ΣHCH and PCBs were found in all the samples analysed. In general, the pattern of contamination with these organochlorine chemicals followed the order of ΣDDT > PCBs > ΣHCH with some prominent levels of ΣDDT.

Cultivated soil samples recorded the highest DDT level of 290 ng/g in a sugarcane field (sample No. 7). On the other hand, non-cultivated soils reached the highest level of 38 ng/g in a school grounds (sample No. 19). Moreover, higher concentrations of ΣDDT were found in field crop soil samples other than paddy field soils (Table 1, Table 2 and Figure 2). It might be attributed to the larger quantity of DDT used for protecting crops from pests. Information on DDT production and consumption in Vietnam is not available. An

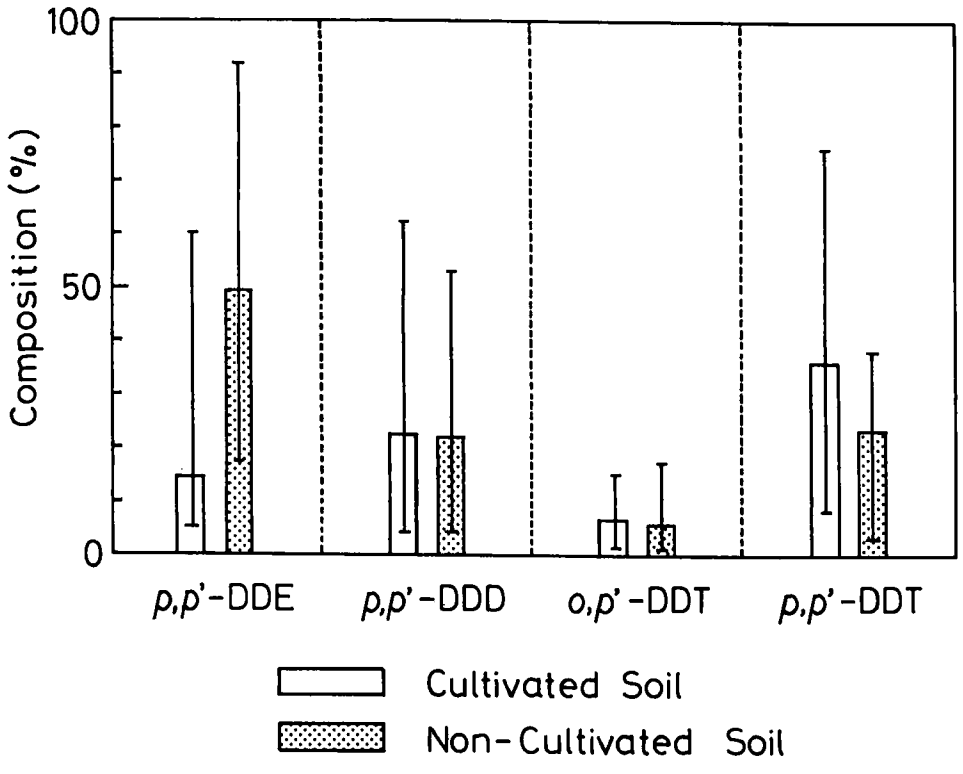


Figure 4 Percentage composition of DDT metabolites in the analysed soil samples.

earlier study[8] has reported high concentrations of ΣDDT in soil samples from many places throughout Vietnam. Schecter et al.[10] reported the presence of very high levels of DDTs in human breast milk from Vietnam. Similarly, Schecter et al.[11] and Kannan et al.[7] found high residues of DDTs in foodstuffs from Vietnam. These results coupled with the data from the present study suggest that the existence of DDT in Vietnam's environment is due to its large scale usage nationwide. However, differences of DDT concentrations in soils were remarkable among different sampling sites.

Concentrations of ΣDDT in cultivated soils from the provinces of Tayninh and Songbe (ranging from 1.0 to 290 ng/g with mean value of 74 ng/g) were comparable with those from other places in Vietnam recorded in a previous study[8]. On the other hand, these levels were lower than those reported for cultivated soils from India[12] but were apparently higher than those detected in cultivated soils from other tropical Asian countries like Thailand and Taiwan[8]. Similarly, DDT concentrations in non-cultivated soils from the two provinces were lower than those from India[12] but higher than those reported for non-cultivated soils from Thailand and Taiwan[8] (see Table 3).

The composition of DDT metabolites in most of cultivated and non-cultivated soil samples showed higher percentage of *p,p'*–DDE than *p,p'*–DDD or *p,p'*–DDT (Fig. 4). In

Table 3 Concentrations (ng/g, dry wt) of ΣDDT and ΣHCH reported from various tropical Asian countries (figures in parentheses are mean values).

Country	*Survey year*	*Σ DDT*	*Σ HCH*	*Reference*
Cultivated Soil				
India	1988	0.85–4,400 (390)	0.42–86,100 (2,000)	12
Indonesia	1982	0–20 (1.0)	0.5–20 (9.9)	25
Taiwan	1990	2.4–78 (23)	0.33–1.9 (0.91)	8
Thailand	1988,1990	0.5–98 (8.8)	0.1–1.6 (0.44)	8
Vietnam	1990	0.73–1,300 (110)	0.15–55 (4.8)	8
Vietnam	1991	1.0–290 (73)	0.09–2.3 (0.88)	Present study
Non-cultivated Soil				
India	1988	3.4–190 (61)	0.55–27 (16)	12
Taiwan	1990	4.2–31 (17)	0.85–4.8 (2.1)	8
Thailand	1988	2.4–4.9 (3.7)	0.07–0.08 (0.75)	8
Vietnam	1991	0.25–38 (9.6)	0.09–2.1 (0.94)	Present study

contrast with the results obtained from a study under reductive temperate conditions, where *p,p'*–DDD was found to be the main residual component among DDTs[13], results from this work have shown that under tropical conditions *p,p'*–DDE is the predominant metabolite of DDTs in soil. This is in good agreement with the studies of Ramesh et al.[14] and Kawano et al.[12] reporting that *p,p'*–DDE was a major breakdown product of DDT in soil samples from different places in India. However, the content of *p,p'*–DDT was the highest among all DDT compounds in a few other locations. This reflects the continuing input of technical DDT formulation into the soils.

With regards to HCHs, low concentrations were recorded in both cultivated and non-cultivated soil samples (Table 2 and Figure 3). These low levels suggest that HCHs were used in small quantity or only deposited into the soils by aerial fallout particles. Furthermore, high possibility of HCH dissipation by atmospheric transport should be taken into account for the result. Kaushik[15] in an experiment under sub-tropical conditions reported that 90 days after application, the losses mainly due to volatility of HCH applied to cultivated and non-cultivated soil plots were 99.1% and 96.8% of the initial concentrations, respectively, in the 7.5cm upper layers. Takeoka et al.[16] and Tanabe et al.[17] in other studies conducted in south India have shown the same trend. These imply that the influx of the insecticide from applied sites to the atmosphere is of the most concern.

In comparison with other places, HCH residues determined in this study were as low as those recorded in soils from Thailand and Taiwan, and apparently far lower than those reported elsewhere, even other places of Vietnam (Table 3).

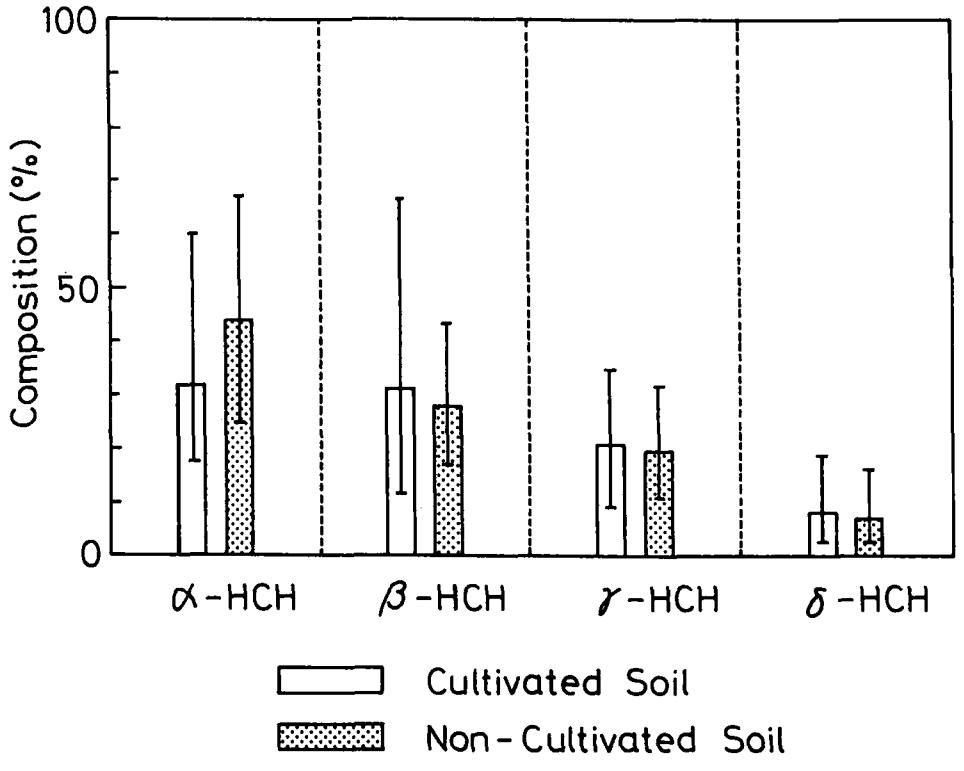


Figure 5 Percentage composition of HCH isomers in the analysed soil samples.

Isomer percentage composition of HCHs exhibited highest levels of α– followed by β–, γ–, and δ–HCH in this order (Figure 5). Largest quantity of α–HCH in technical grade HCH[18] which may have been applied to the soils, could explain its high percentage in the residues detected. On the other hand, β–HCH presented higher proportion than γ–HCH in the residues determined though the former is smaller than the latter in technical grade HCH. This is due to the differences of their physico-chemical properties. It has been documented that β–HCH has the lowest vapour pressure and water solubility as compared to other HCH isomers but is the most stable and relatively resistant to microbial degradation[19].

Considerable PCB residues could be detected in both cultivated and non-cultivated soil samples with less marked differences (Table 2 and Figure 6). In most soil samples , PCB levels exceeded those of ΣHCH (Table 2). The concentrations of PCBs ranged from 0.45 to 150 ng/g in cultivated soil samples while that in non-cultivated ones were from 0.23 to 92 ng/g. The two highest levels were found in the samples of a crop field (sample No. 11) and a former U.S. air base grounds (sample No. 16) . In an earlier study[8] a high PCB concentration (350 ng/g) was recorded in a paddy field soil sample from the same area in Tayninh province. Vietnamese foodstuffs purchased from Tayninh province also revealed high degree of PCB contamination[7]. These high levels are unusual for a rural area in a less developed country.

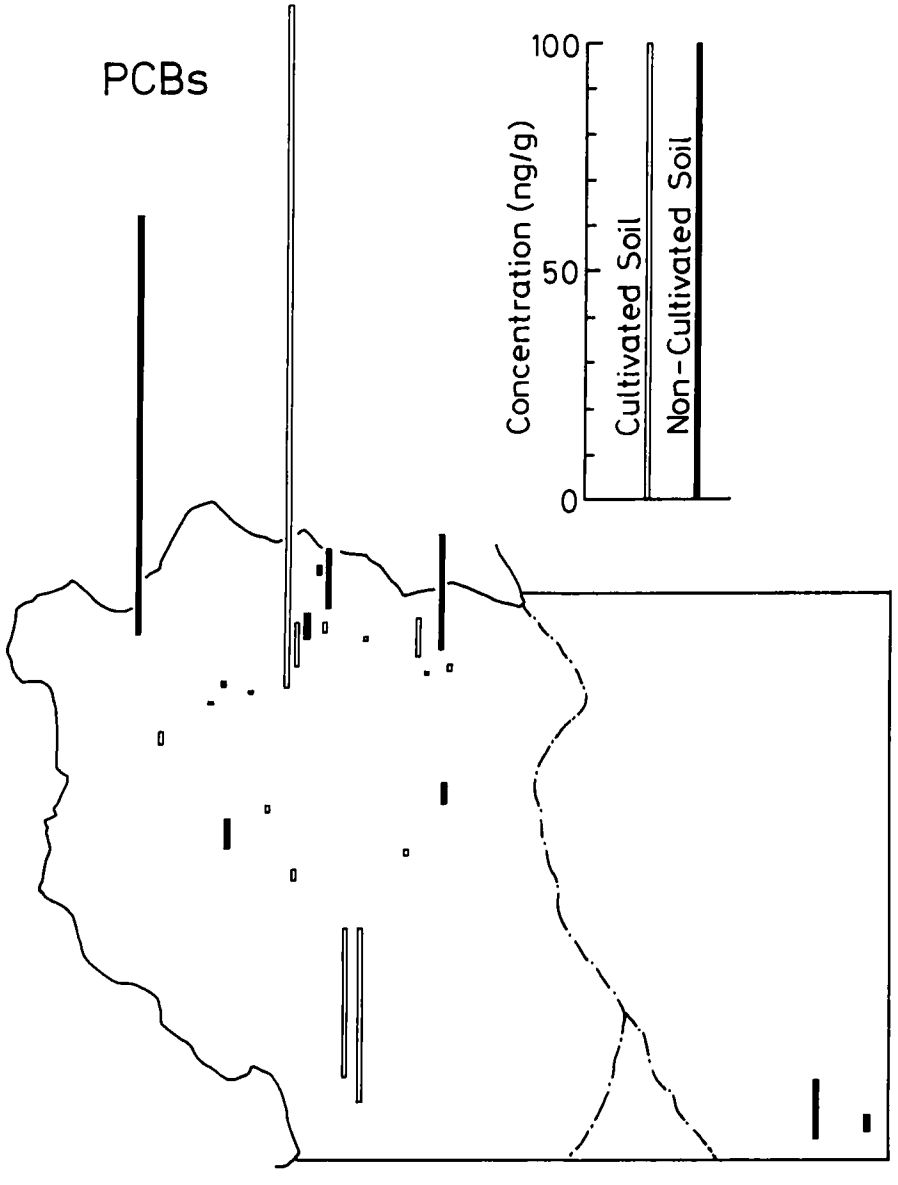


Figure 6 Spatial distribution of PCBs in soils from Tayninh and Songbe, Vietnam.

The Second Indochina War or Vietnam conflict which lasted from 1961 to 1975 is noted for the innovative use of modern technologically advanced weapons and methods including massive rural area bombing, extensive chemical and mechanical forest destruction, wide-ranging chemical anti-personel harassment and area denial and enormous forced population replacements[20]. Though there has not been any documentary evidence for the usage of PCBs in the war, the fact that PCBs were actively used in the military operations can not be ruled out. During the war many kinds of weapons, chemicals, vehicles and warfare equipments were employed. As the most successful products for many industrial purposes, especially in the 1960's and early 1970's, PCBs could have been used in the above mentioned military activities. The provinces of Tayninh and Songbe were among the worst hit areas by such activities[20,21] which could have resulted in the release of PCBs to the environment recording high levels in the soils. For example, higher proportions of PCBs out of total organochlorines (ΣDDT, ΣHCH and PCBs) were found in the samples (Nos. 6, 16, 18, 21) collected from the area which was sprayed with highest doses by herbicides and defoliants[21].

As mentioned earlier, high levels of PCB residues were found in both cultivated and non-cultivated soil samples. It might be due to the fact that many non-cultivated sites used for military activities in those years (for instance, battlefields , bombed and chemical-sprayed areas, military bases, etc ..) have been converted to agricultural fields in recent years. Moreover, during war time, agricultural lands were also seriously affected.

Besides, some electrical goods containing PCBs have been imported in Vietnam from foreign countries, for instance, from Australia[22]. In addition to the PCBs already released into the environment, those being used in transformers, capacitors and other electric appliances could also form another source of PCB contamination.

The mean PCB concentration in soils (17 ng/g) obtained in this study was comparable with those of the earlier reported Vietnamese (25 ng/g)[8] and Japanese soils (37 ng/g)[13], but lower than those reported for soils from Taiwan (95 ng/g)[8], and America or Canada, (100 ng/g)[23] where the reported values indicated for developed nations reveal the amount observed during the period of PCBs usage and disposal.

From the results of this study it is obvious that DDT is still being used in Vietnam including Tayninh and Songbe provinces, resulting in soil contamination. On the other hand, there is little contamination of soils with HCHs in the two provinces studied. PCB contamination of soils in the two provinces is noticeable especially in northern districts of the province of Tayninh. Thus, even in the tropics where rapid volatilization of residues is favourable, largescale usage and disposal of the chemicals can lead to prominent soil contamination. Consequently, the residues will get into food chain and affect human health. Considerable levels of organochlorine insecticides were found in plants due to uptake from soil[24]. Many agricultural products from Vietnam have been noted to be contaminated by DDTs, HCHs and PCBs[7]. These results point out another contamination route of humans from polluted soils.

In order to make clear the major sources of PCB contamination in the Vietnamese environment, it is necessary to conduct further research. During the course of this investigation, many unknown peaks have been recorded in the chromatograms. This indicates that apart from known organochlorines, other chemicals which are suspected to be persistent, also exist in soils from Vietnam. This offers another challenging area for research.

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