Bull Environ Contam Toxicol (2009) 82:516–521
DOI 10.1007/s00128-008-9629-9

Residue, Temporal Trend and Half-Life Time of Selected Organochlorine Pesticides (OCPs) in Surface Soils from Bacninh, Vietnam

**Vu Duc Toan · Vu Duc Thao · Jürg Walder ·
Cao The Ha**

Received: 16 June 2008 / Accepted: 12 December 2008 / Published online: 23 January 2009

Abstract Selected organochlorine pesticides (p,p'-DDT, p,p'-DDE, p,p'-DDD, $\alpha,\beta,\gamma,\delta$-HCH) were analyzed in the surface soils of Bacninh, Viet Nam. Forty representative soil samples were collected from Bacninh town and three surrounding districts. ΣDDT concentrations ranged from <0.02 to 160.86 ng g^{-1} dry weight, whereas ΣHCH concentrations ranged from <0.05 to 9.54 ng g^{-1} dry weight. The half-life times of ΣDDT and ΣHCH are 6.7 and 4.9 years, respectively. The decreasing trends of ΣDDT and ΣHCH levels during the period from 1992 to 2006 are observed. There is no recent input of DDT and HCH in the study area.

Keywords Organochlorine pesticides · Soil · Temporal trend · Half-life

Of all the chemical compounds with a serious potential environmental impact, organochlorine pesticides (OCPs) have received the most attention. Studies in human provide supporting evidents for potential carcinogenic effects of OCPs. They can transport over long distance and accumulate in soil, water and tissues of living organisms. In order to protect human health and environmental quality, many nations in the World has signed the Stockholm Convention which aims at complete elimination of OCPs impact. Vietnam, like other developing countries, faces many pesticide problems. Certain kinds of OCPs such as dichlorodiphenyltrichloroethane (DDT) and hexachlorocyclohexane (HCH) have been used in the country in considerable amounts as pesticides for crop protection and as vector control for public health purposes. According to the survey carried out by Vietnam Environment Protection Agency in 2006, the total amount of organochlorine pesticides in the entire country is approximately 300 tonnes, whereas the total amount of DDT and HCH is approximately 10 tonnes (VEPA 2006). Bacninh province, located in the Red River delta, is a typical centre of industrial, agricultural and traditional village in Viet Nam. According to the study of Thao and Toan (2005), significant residues of DDT and HCH were detected in surface soil from Bacninh. It clearly indicated their long-term use in this province. However, to our knowledge, few data are available for the composition analysis, the temporal trend and half-life time of DDT and HCH in the surface soils from Bacninh. The present study aims at assessing the residue of DDT and HCH in the surface soil from Bacninh to fill this gap.

Materials and Methods

The sampling was carried out in February 2006, during the dry season. Forty samples from the upper 5 cm of the soil were collected from both agricultural areas and traditional villages in Bacninh town, as well as from three surrounding districts (TuSon, TienDu and YenPhong). The soil samples

V. D. Toan (✉)
Hanoi Water Resources University, 175 Tay Son Street,
Hanoi, Vietnam
e-mail: vuductoan2001@yahoo.com; vuductoan@wru.edu.vn

V. D. Thao
Hanoi University of Technology, 1 Dai Co Viet Street,
Hanoi, Vietnam

J. Walder
University of Applied Sciences North-Western Switzerland,
Gründenstrasse 40, Muttenz CH-4132, Switzerland

C. T. Ha
Research Centre for Environmental Technology and Sustainable
Development, 334 Nguyen Trai Street, Hanoi, Vietnam

were marked from A1 to A40. The sampling locations were chosen at random in February 2006, with an attempt to get them evenly distributed over selected region of Bacninh (approximately 800 km^2, about one million people, Fig. 1). Each sample was a mixture of five sub-samples (four in the corners of a rectangle and one in the crossing point of two diagonals). The samples were taken with solvent-rinsed stainless steel scoops from the upper 5 cm of the soil and then transferred to pre-cleaned polyethylene bags. The collected samples were air dried at room temperature (22–25°C), ground and sieved through a steel mesh (1 mm grid size). All samples were homogenised and maintained at 4°C until analysis.

Selected OCPs were analyzed following the method described by Thao et al. (1993). Briefly, about 20 g of soil sample was wetted by distilled water and then extracted three times in a shaker, each time with 100 ml acetone for 30 min.

Hundred millilitres of distilled water was added to the acetone extract and was extracted again three times, each time with 100 ml *n*-hexane for 30 min. After that, the *n*-hexane extract was combined, dried by passing through anhydrous sodium sulphate and concentrated to around 5 ml. The extract is continued to clean up with 8 g of activated Florisil packed in a glass column. The first fraction eluted by *n*-hexane contained *p,p′*-DDE and polychlorobiphenyls (PCBs). PCBs were also analyzed to mention in another study by the author. The second fraction eluted with 20% dichloromethane in *n*-hexane contained HCH ($\alpha,\beta,\gamma,\delta$) isomers, *p,p′*-DDD and *p,p′*-DDT. Each fraction was concentrated to 10 ml, sulphur removed with activated copper chips and treated with concentrated sulphuric acid. Final extracts were concentrated to 5 ml by a rotary vacuum evaporator and then to around 300 μL under a gentle stream of purified nitrogen.

The samples were analyzed with the gas chromatograph (Varian Star 3400Cx) equipped with DB5 column (30 m length × 0,32 i.d. mm × 0,25 μm film thickness), mass spectrophotometer (Varian Saturn 2000) and automatic injector (Varian 8200Cx). The residue levels of DDT and HCH were determined by the external standard method using peak areas. The standard mixture containing $\alpha,\beta,\delta,\gamma$-HCH isomers, *p,p′*-DDE, *p,p′*-DDD, *p,p′*-DDT with a concentration of 200 ng μL^{-1} per compound was purchased from Supelco Chemical Co., Germany. Linear calibration curves over six calibration levels for all analyzed compounds were obtained acceptable limits of the linearity criterion. ΣDDT was determined as the sum of *p,p′*-DDE, *p,p′*-DDD and *p,p′*-DDT, whereas ΣHCH was determined as the sum of α,β,γ and δ isomers. The method detection limits of the selected OCPs were calculated from real soil samples as three times the signal/noise ratio and were 0.02 ng g^{-1} dry weight for *p,p′*-DDT, *p,p′*-DDD and *p,p′*-DDE, 0.05 ng g^{-1} dry weight for α-HCH, β-HCH, γ-HCH, and δ-HCH. One procedural blank was run for every set of five samples to check for secondary contamination. The recoveries of α-HCH, β-HCH, γ-HCH, δ-HCH, *p,p′*-DDE, *p,p′*-DDD and *p,p′*-DDT with spiked soil samples from Bacninh ranged from 82 to 98%. The calculated concentrations of selected OCPs were not corrected for recoveries. Duplicates of soil samples were also performed and relative standard deviations were less than 15%. All concentrations were calculated with respect to the dry weight of soil samples.

Results and Discussion

The selected OCPs concentrations in the collected soil samples are shown in Table 1. ΣDDT and ΣHCH were detected in 29 of 40 soil samples. Significant ΣDDT concentrations were found in most agricultural areas in Bacninh. The ΣDDT concentrations ranged from <0.02 to 160.86 ng g^{-1} with a mean 106.79 ± 37.12 ng g^{-1}. The

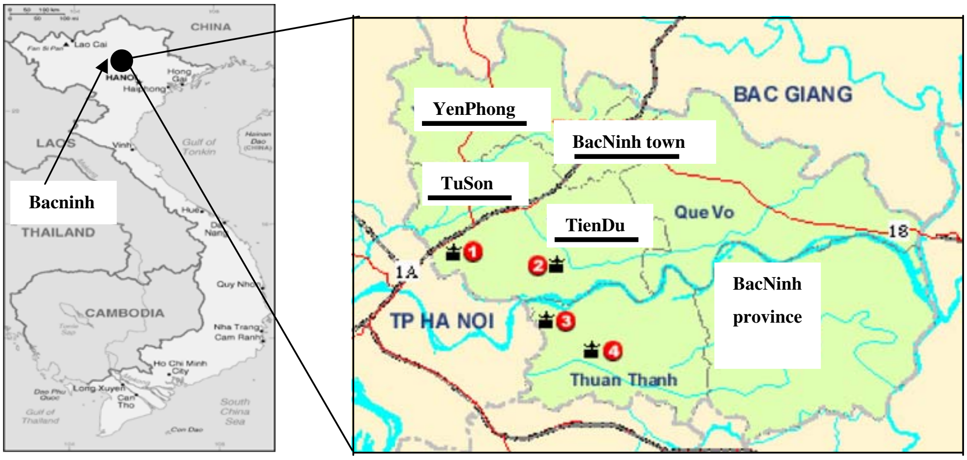

Fig. 1 Map of the study area

Table 1 Concentrations of selected OCPs (ng g^{-1}) in the surface soil from Bacninh

Location	α-HCH	β-HCH	γ-HCH	δ-HCH	ΣHCH	p,p'-DDE	p,p'-DDD	p,p'-DDT	ΣDDT
Agricultural areas									
TuSon 1[a]									
A1	3.97	4.16	0.75	0.57	9.45	79.38	45.32	36.16	160.86
A2	3.76	3.96	0.56	0.28	8.56	76.34	42.82	33.49	152.65
A3	3.46	3.85	0.69	0.17	8.17	49.46	25.32	23.67	98.45
A4	2.38	4.56	0.66	0.16	7.76	48.44	24.97	23.35	96.76
A5	3.18	3.49	0.66	0.93	8.26	79.68	45.49	36.29	161.46
A6	2.75	2.77	0.88	0.85	7.25	43.67	21.58	21.32	86.57
A7	<0.05	<0.05	<0.05	<0.05	<0.05	<0.02	<0.02	<0.02	<0.02
A8	3.15	3.87	0.66	0.59	8.27	48.65	24.77	23.36	96.78
TienDu 1									
A9	3.09	3.35	0.97	0.95	8.36	42.56	24.04	20.07	86.67
A10	3.26	4.07	1.05	0.99	9.37	70.45	39.63	36.18	146.26
A11	4.05	4.75	0.57	0.09	9.46	69.52	37.35	35.28	142.15
A12	3.56	3.97	1.17	0.87	9.57	65.88	35.27	31.09	132.24
A13	3.86	3.98	0.75	0.99	9.58	63.19	34.15	31.29	128.63
A14	3.77	3.58	0.67	0.65	8.67	59.25	32.17	30.92	122.34
A15	3.19	3.76	0.85	0.78	8.58	58.35	31.23	26.56	116.14
Bacninh town 1									
A15	1.89	2.05	0.45	0.49	4.88	14.49	7.24	4.89	26.62
A17	1.88	2.07	0.55	0.46	4.96	51.65	35.43	25.54	112.62
A18	2.36	2.96	0.48	0.98	6.78	52.48	32.32	29.76	114.56
A19	1.47	2.26	0.49	0.47	4.69	47.26	29.54	25.67	102.47
YenPhong 1									
A20	3.08	3.46	0.85	0.89	8.28	48.77	27.47	20.19	96.43
A21	2.16	2.86	0.57	0.38	5.97	48.46	24.55	20.68	93.69
A22	2.58	3.06	0.76	0.58	6.98	53.65	28.25	22.85	104.75
A23	2.08	2.96	0.56	0.69	6.29	52.26	28.18	21.39	101.83
A24	2.85	3.09	0.58	0.35	6.87	44.29	19.76	18.29	82.34
Town and traditional villages									
TuSon 2[b]									
A25	<0.05	<0.05	<0.05	<0.05	<0.05	<0.02	<0.02	<0.02	<0.02
A26	<0.05	<0.05	<0.05	<0.05	<0.05	<0.02	<0.02	<0.02	<0.02
A27	1.38	1.49	0.36	0.25	3.48	19.98	11.24	8.23	39.45
A28	2.27	2.58	0.66	0.35	5.86	17.82	6.14	3.58	27.54
TienDu 2									
A29	1.79	1.98	0.45	0.35	4.57	17.86	8.24	6.44	32.54
A30	1.56	1.89	0.45	0.28	4.18	17.86	9.89	7.09	34.84
A31	1.06	1.35	0.29	0.28	2.98	16.74	9.78	8.02	34.54
A32	<0.05	<0.05	<0.05	<0.05	<0.05	<0.02	<0.02	<0.02	<0.02
A33	<0.05	<0.05	<0.05	<0.05	<0.05	<0.02	<0.02	<0.02	<0.02
Bacninh town 2									
A34	<0.05	<0.05	<0.05	<0.05	<0.05	<0.02	<0.02	<0.02	<0.02
A35	<0.05	<0.05	<0.05	<0.05	<0.05	<0.02	<0.02	<0.02	<0.02
A36	1.56	1.75	0.39	0.49	4.19	12.86	6.24	5.37	24.47
A37	<0.05	<0.05	<0.05	<0.05	<0.05	<0.02	<0.02	<0.02	<0.02
A38	<0.05	<0.05	<0.05	<0.05	<0.05	<0.02	<0.02	<0.02	<0.02

Table 1 continued

Location	α-HCH	β-HCH	γ-HCH	δ-HCH	ΣHCH	*p,p′*-DDE	*p,p′*-DDD	*p,p′*-DDT	ΣDDT
YenPhong 2									
A39	<0.05	<0.05	<0.05	<0.05	<0.05	<0.02	<0.02	<0.02	<0.02
A40	<0.05	<0.05	<0.05	<0.05	<0.05	<0.02	<0.02	<0.02	<0.02

[a] TuSon 1: Agricultural areas of TuSon

[b] TuSon 2: town and traditional villages of TuSon

mean ΣDDT concentration in agricultural areas in Bacninh was higher than maximal allowable concentration (MAC) in surface soil according to the Vietnamese standard 5941-1995 (ΣDDT < 100 ng g^{-1}). The results point out the common usage of DDT as pesticides for crop protection in these sites. Because the usage of DDT in Vietnam was banned in 1994, this clearly indicates that the residues of DDT are a result of the use of such compounds over the last decades. In non-agricultural areas such as town and traditional villages, ΣDDT was also detected, which ranged from <0.02 to 39.45 ng g^{-1} with a mean 12.09 ± 16.42 ng g^{-1}). It might be a results of DDT used as a vector control for public health purposes in these areas. According to Hung and Thiemann (2002), 24,042 tonnes of technical DDT were used against malaria and mosquitoes from 1957 to 1994 in Vietnam.

With regards to ΣHCH, low concentrations were detected in the analyzed soil samples. The ΣHCH concentrations in agricultural areas ranged from <0.02 to 9.54 ng g^{-1} (mean 7.38 ± 2.17 ng g^{-1}), while those from Bacninh City and traditional villages ranged from <0.02 to 5.86 ng g^{-1} (mean 1.58 ± 2.18 ng g^{-1}). In comparison with the Vietnamese standard 5941-1995, γ-HCH concentrations in the analyzed soil were also much lower than MAC (γ-HCH <100 ng g^{-1}). Similar to DDT, the contamination of HCH originated in the usage as pesticides for crop protection and as vector control for public health purposes. HCH was also probably deposited into the urban areas by atmospheric transport from agricultural areas. From the surface soil in the agricultural areas, HCH may be accumulated in food chain and then in human body. Therefore, although their concentrations were low, the presence of HCH in most soil samples is clearly marked. When compared with other regions in the world, the obtained ΣDDT concentrations in Bacninh are comparable with those in soil of Shanghai, China (18–142 ng g^{-1}) and lower than Tasman, New Zealand (30–34,500 ng g^{-1}) (Nakata et al. 2005; Gaw et al. 2006). Meanwhile, the obtained ΣHCH concentrations in Bacninh are lower than those in soil Tanzania (<0.1–59 ng g^{-1}) and higher than residues found in Shanghai, China (<0.03–2.4 ng g^{-1}) (Kishimba et al. 2004; Nakata et al. 2005).

Besides the contamination status of selected OCPs, the analysis of their composition is useful to understand their patterns as well as possible contaminant sources. The order of mean percentages of DDT and its metabolites in soil samples from Bacninh was *p,p′*-DDE (50.4%) > *p,p′*-DDD (29.4%) > *p,p′*-DDT (20.1%). It should be noted that DDT can be biodegraded in the environment to DDD under anaerobic conditions and to DDE under aerobic conditions. During the dry season, in northern Vietnam, with aerobic conditions, the active oxidative transformation of *p,p′*-DDT to *p,p′*-DDE is facilitated and creates a larger percentage of *p,p′*-DDE than the other components of ∑DDT. This is in good agreement with the research by Ramesh et al. (1991) in tropical regions reporting that *p,p′*-DDE was a major breakdown product of DDT in soil from different places in India. With regards to DDT metabolites, the ratio of (*p,p′*-DDE + *p,p′*-DDD)/ΣDDT in the soil samples from Bacninh ranged between 0.74 and 0.87 (mean 0.77). This indicates that the degradation of DDT occurred significantly and there is no recent input of DDT in the study areas.

Technical HCH and lindane (>99% γ-HCH) have been officially banned since 1994 in Vietnam. The mean percentages of HCH isomers in analyzed soil samples from Bacninh followed the order β-HCH (44.4%) > α-HCH (37.9%) > γ-HCH (9.4%) > δ-HCH (8.3%). Among the isomers, β-HCH has the lowest water solubility and vapour pressure. It is the most stable isomer and is relatively resistant to microbial degradation. Besides that, there is the isomerisation of α- to β-HCH and of γ- via α- to the more stable β-HCH, which is energetically more favourable in the environment (Manz et al. 2001). Therefore, the predominance of β-HCH reflects an old source of input of HCH in the environment. Low ratios of α-HCH/γ-HCH may represent the use of lindane, whereas high ratios of these isomers may depict the use of technical HCH. Measured results of McConnell et al. (1993) show that the ratio of α-HCH/γ-HCH in areas where lindane has been typically used ranges from 0.2 to 1, compared to a range of 4–15 for technical HCH. Here, the ratios of α-HCH/γ-HCH in the analyzed soil samples from Bacninh range from 3.1 to 7.1 (mean 4.1). This result confirmed the use of technical HCH as the major source and lindane as the minor source in the study areas.

With regards to concentrations of selected OCPs in soil samples from Bacninh reported in these other researches, their temporal trend could be displayed. It was reported that the mean concentration of $\sum$DDT in soil samples from Bacninh in 1992 (10 soil samples), in 1995 (10 soil samples), in 1998 (10 soil samples), in 2001 (10 soil samples) and in 2006 (60 soil samples) are 278.06, 254.73, 156.46, 124.85, and 68.92 ng g^{-1}, respectively, (Thao and Toan 2005; this study). In case of $\sum$HCH, the mean concentration in soil samples from Bacninh in 1992 (10 soil samples), in 1995 (10 soil samples), in 1998 (10 soil samples), in 2001 (10 soil samples) and in 2006 (60 soil samples) are 33.86, 29.96, 17.46, 11.85, and 5.06 ng g^{-1}, respectively, (Thao and Toan 2005; this study). The decreasing trend of $\sum$DDT and $\sum$HCH concentration can clearly be seen. In general, the total temporal trend of selected OCPs can be divided into two trends. The first trend is an increase of the concentrations of selected OCPs when their sources continue to penetrate in the environment. The second trend is a decrease of the concentrations when the dissipation of selected OCPs took place. Therefore, the significant decreasing trend of ΣDDT and ΣHCH reflects that their dissipations took place for a long time, whereas the new contaminative sources are limited. Because Vietnam has banned the use of DDT and HCH, there is high possibility that these trends may continue in the future.

According to the environmental protection agency of the United Nations, half-life ($t_{1/2}$) is the time required for a concentration of a substance to be reduced to one-half. This parameter is different from the 50% dissipation time (DT_{50}), which is defined as the amount of time required for 50% of the initial concentration of a substance to dissipate. When the reaction follows first-order degradation kinetics, the half-life will be equivalent to the 50% dissipation time. When the degradation rate is not first-order, the half-life and the 50% dissipation time will differ. Regarding these definitions, it is complicated to determine exact half-life values of ΣDDT and ΣHCH. Nevertheless, the estimated half-life time is fairly beneficial for assessing the trend of contamination of these compounds in the future. Approximately, the disappearance of ΣDDT and ΣHCH from the surface soil layer can be described by a simple first-order model (Bi et al. 2002):

$$C_t = C_0 \mathrm{Exp}(-kt)$$

$$\ln C_t = \ln C_0 - kt = \ln C_0 - k(y - y_0) = (\ln C_0 + y_0) - ky$$

where C_0 is the initial mean concentration of selected OCPs from the surface soil; C_t is the mean concentration of selected OCPs from the surface soil at time t (year); y is the sampling year. y_0 is the year when the substance begins to penetrate into the soil sampling sites. k is first-order rate constant for disappearance of selected OCPs from the surface soil.

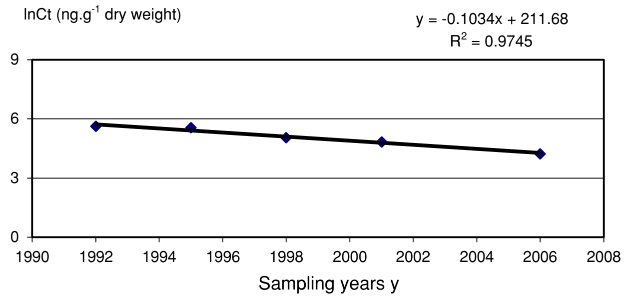

Fig. 2 Relation between ln C_t, $_{\Sigma\mathrm{DDT}}$ and sampling years

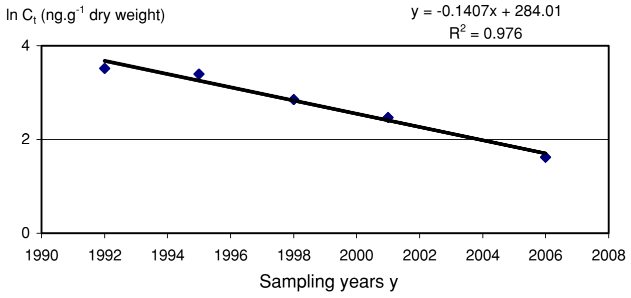

Fig. 3 Relation between ln C_t, $_{\Sigma\mathrm{HCH}}$ and sampling years

The half-life ($t_{1/2}$) is calculated from k by formula: $t_{1/2} = \ln 2/k$. The linear curves between lnC_t and y are built by using the mean concentrations of ΣDDT and ΣHCH in the surface soil from Bacninh as well as the sampling years (Thao and Toan 2005; this study).

Based on the angular coefficients in Figs. 2 and 3, the estimated half-life time of ΣDDT and ΣHCH from soil in study areas are 6.7 and 4.9 years. The persistence of DDT and HCH in soil is highly variable and strongly depends on the soil type as well as the conditions of the environment. Dissipation is much greater in tropical than in temperate regions. Due to the tropical climate in Vietnam, the average temperature and moisture content in soil are higher than temperate areas and can accelerate the degradation of the study compounds.

Acknowledgments The author would like to thank the Institute for Ecopreneurship and the Institute of Chemistry and Bioanalytics, University of Applied Sciences North-western Switzerland for their support.

References

Bi XH, Chu SG, Meng QY, Xu XB (2002) Movement and retention of polychlorinated biphenyls in a paddy field of WenTai area in China, Agriculture. Ecosyst Environ 89:241–252. doi:10.1016/S0167-8809(01)00210-9

Gaw SK, Wilkins AL, Kim ND, Palmer GT, Robinson P (2006) Trace element and ΣDDT concentrations in horticultural soils from the Tasman, Waikato and Auckland regions of New Zealand. Sci Total Environ 355:31–47. doi:10.1016/j.scitotenv.2005.02.020

Hung DQ, Thiemann W (2002) Contamination by selected chlorinated pesticides in surface waters in Hanoi, Vietnam. Chemosphere 47:357–367. doi:10.1016/S0045-6535(01)00342-3

Kishimba MA, Henry L, Mwevura H, Mmochi AJ, Mihale M, Hellar H (2004) The status of pesticide pollution in Tanzania. Talanta 64:48–53. doi:10.1016/j.talanta.2003.11.047

Manz M, Wenzel KD, Dietze U, Schüürmann G (2001) Persistent organic pollutants in agricultural soils of central Germany. Sci Total Environ 277:187–198. doi:10.1016/S0048-9697(00)00877-9

McConnell LL, Cotham WE, Bidleman TF (1993) Gas exchange of hexachloro cyclohexane in the Great Lakes. Environ Sci Technol 27:1304–1311. doi:10.1021/es00044a003

Nakata H, Hirakawa Y, Kawazoe M, Nakabo T, Arizono K, Abe SI, Kitano T, Shimada H, Watanabe I, Li W, Ding X (2005) Concentrations and compositions of organochlorine contaminants in sediments, soils, crustaceans, fishes and birds collected from Lake Tai, Hangzhou Bay and Shanghai city region, China. Environ Pollut 133:415–429. doi:10.1016/j.envpol.2004.07.003

Ramesh A, Tanabe S, Murase H, Subramanian AN, Tatsukawa R (1991) Distribution and behavior of persistent organochlorine insecticides in paddy soil and sediments in the tropical environment: a case study in South India. Environ Pollut 74:293–307. doi:10.1016/0269-7491(91)90077-A

Thao VD, Toan VD (2005) Time trend variation of persistent organochlorine residues in soils from Vietnam, Regional Symposiums on Chemical Engineering, November Hanoi, Vietnam, pp 351–360

Thao VD, Kawano M, Tatsukawa R (1993) Persistent organochlorine residues in soils from tropical and sub-tropical Asian countries. Environ Pollut 81:61–71. doi:10.1016/0269-7491(93)90029-N

Vietnam Environment Protection Agency (VEPA) (2006) Ke hoach Quoc gia xu ly chat o nhiem kho phan huy (in Vietnamese). Available from: http://www.nea.gov.vn/thongtinmt/noidung/vnn_14_08_06.htm. Assessed on 1 March 2008