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Contamination by Selected Organochlorine Pesticides (OCPs) in Surface Soils in Hanoi, Vietnam

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Abstract An evaluation of selected organochlorine pesticide residues [*p,p′*- dichlorodiphenyltrichloroethane (DDT), *p,p′*- dichlorodiphenyldichloroethylene (DDE), *p,p′*- dichlorodiphenyldichloroethane (DDD), α, β, γ and δ- hexachlorocyclohexane (HCH)] in the surface soils of Hanoi, Vietnam was carried out. Sixty representative soil samples were collected from the centre of Hanoi and five surrounding districts. In agricultural areas, ΣDDT concentrations ranged from < 0.02 to 171.83 ng g^{-1} (mean 89.86 ng g^{-1}) dry weight, whereas ΣHCH concentrations ranged from < 0.05 to 20.57 ng g^{-1} (mean 8.03 ng g^{-1}) dry weight. Investigation of the ratio of different isomers in the soil samples indicates that there has been no recent input of DDT and HCH in the study area.

Keywords Contamination · DDT · HCH · soil

Of all the chemical compounds with a potential environmental and human health impact, organochlorine pesticides (OCPs) have received the most attention. Concern about the toxicology of these compounds has led to international efforts to control their use and disposal. Research projects have led to a deeper understanding of the contamination as well as the fate and behavior of OCPs in the environment.

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 vector control for public health purposes. Farmers and other pesticide users usually ignored the risks, safety instructions and essential protective measures. Hanoi city, which is located in the Red River delta in the north of Vietnam, is the centre of culture, politics, economy and trade for the whole country. Hanoi is composed of the centre and five suburban districts, SocSon, DongAnh, GiaLam, TuLiem and ThanhTri, with many factories and agricultural areas. Recent studies have been conducted in order to determine the concentrations of selected OCPs in sediment, molluscs, surface water and human breast milk from Hanoi (Nhan et al., 2001; Hung et al., 2002; Minh et al., 2004). In these studies, DDT and its primary metabolites (DDE and DDD) as well as the main HCH isomers (α, β, γ, δ), were detected in all the environmental areas listed above. These studies clearly indicated their long-term use in the city. However, to our knowledge, little data is available concerning DDT and HCH contamination in the surface soils of Hanoi. The present study aims to assess the levels and distribution of these selected OCPs in the surface soil of Hanoi to fill this gap.

Materials and Methods

The sampling was carried out in February 2006, during the dry season. Sixty soil samples were collected from both

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agricultural and industrial areas and from towns in all five suburban districts, as well as from the centre of Hanoi. The soil samples were coded C1 to C60. The sampling sites were chosen at random yet evenly distributed over Hanoi city (approximately 92 1km^2, about 3 million people, Fig. 1). Each sample was a mixture of five subsamples (four in the corners of a rectangle and at in the crossing point of the two diagonals). The samples were taken with solvent-rinsed stainless-steel scoops from the upper 5 cm of the soil and then transferred to precleaned 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 homogenized and maintained at 4°C until analysis.

Selected OCPs were analyzed following the method described by Thao et al. (1993). In short, 20 g of soil sample was wetted with distilled water and then extracted three times in a separator funnel, each time with 100 ml of acetone for 30 min. 100 ml distilled water was added to the acetone extract and the resulting solution was again extracted three times, each time with 100 ml *n*-hexane for 30 min. The *n*-hexane extracts were then combined, dried by passing them through anhydrous sodium sulphate and concentrated to around 5 ml. The concentrated extract was filtered through 8 g of activated Florisil packed in a glass column. The first fraction eluted by 45 ml of *n*-hexane contained *p,p′*-DDE and Polychlorobiphenyls (PCBs). PCBs were also analyzed for use in another study by the authors. The second fraction eluted with 20% dichloromethane in *n*-hexane contained HCH (α, β, γ, δ) isomers, *p,p′*-DDD and *p,p′*-DDT. Each fraction was de-sulfurated using activated copper chips and finally treated with concentrated sulfuric 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. All chemicals used were of analytical grade and were purchased from Fluka Chemical Co., Switzerland.

The samples were analyzed with a gas chromatograph (Varian Star 3400Cx) equipped with a DB5 column (30 m length × 0.32 i.d. mm × 0.25 μm film thickness), mass spectrometer (Varian Saturn 2000) and autosampler (Varian 8200Cx). The DDT and HCH concentrations were determined by the external standard method. The standard solution containing α, β, δ, γ-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 within the acceptable limits of the linearity criterion.

ΣDDT was the sum of *p,p′*-DDE, *p,p′*-DDD and *p,p′*-DDT, whereas ΣHCH was the sum of the α, β, γ and δ isomers. Selected OCPs recoveries were examined using fortified soil samples from Hanoi which had been prepared according to the method of Aydin et al. (2006). The fortified soil samples were spiked with 40 ng g^{-1} dry weight of each of the selected compound. The recoveries ranged from 82 to 98%. The detection limits of the selected OCPs were calculated from real soil samples as three times the signal-to-noise ratio: 0.02 ng g^{-1} dry weight for *p,p′*-DDT, *p,p′*-DDD and *p,p′*-DDE, and 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 concentrations of the selected OCPs were not corrected for recoveries. Duplicates of the soil samples were also collected and the analyses repeated; the relative standard deviations were less than 15%. All concentrations were calculated with respect to the dry weight of soil samples.

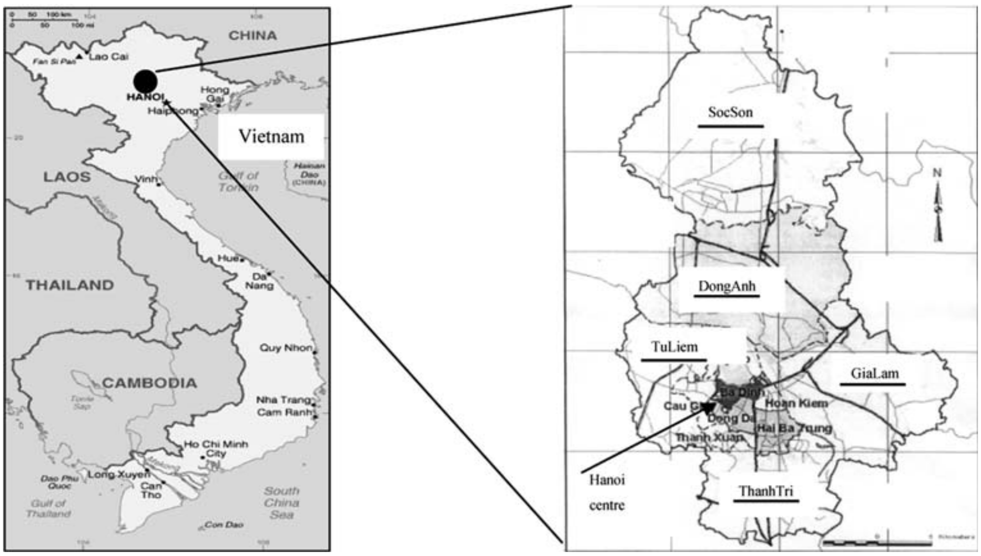

Fig. 1 Map of the study area

Results and Discussion

The concentrations of the selected OCPs in the collected soil samples are all shown in Table 1. The general pattern of contamination followed the order ΣDDT > ΣHCH. ΣDDT was detected in relatively high concentrations in the agricultural areas. The ΣDDT concentrations ranged from <0.02 to 171.83 ng g^{-1}. The mean ΣDDT concentration in the agricultural areas (89.86 ± 47.17 ng g^{-1}) was a little lower than the maximal allowable concentration (MAC) in surface soil according to the Vietnamese standard 5941-1995 (ΣDDT<100 ng g^{-1}). However, the ΣDDT concentrations in some soil samples were still higher than the MAC value. The results show that in the agricultural sampling sites such as C1, C2, C3, C4, C5, C22, C23 and C30, the ΣDDT concentrations were 161.84, 163.75, 102.25, 106.26, 162.76, 168.27, 164.38 and 171.83 ng g^{-1}, respectively (Table 1). These results highlight the common usage of DDT as a pesticide for crop protection at these sites. Because the use of DDT in Vietnam was banned in 1994, this clearly indicates that the ΣDDT residues are a result of the use of this compound over recent decades. In industrial areas, the centre of Hanoi and the towns in the five surrounding suburban districts, ΣDDT was also detected, at levels ranging from <0.02 to 67.82 ng g^{-1} (mean 21.22 ± 22.67 ng g^{-1}). This reflects the use of DDT for vector control for public health purposes in the city. According to Hung et al. (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 <0.05 to 20.57 ng g^{-1} (mean 8.03 ± 3.55 ng g^{-1}), while those from industrial and urban areas ranged from <0.05 to 7.76 ng g^{-1} (mean 3.23 ± 2.85 ng g^{-1}). In comparison with the Vietnamese standard 5941-1995, γ-HCH concentrations in the analyzed soil samples were much lower than the MAC value (γ-HCH<100 ng g^{-1}). Similar to DDT, the HCH contamination originated from its use as a pesticide for crop protection and for vector control for public health purposes.

At present, there is no Vietnamese standard on the MAC value of ΣHCH in surface soil, nor is there official quantitative information on the cumulative use of DDT and HCH in Hanoi. HCH was also probably deposited into the urban areas by atmospheric transport from agricultural areas. From the surface soil in agricultural areas, HCH may be accumulated in the food chain and then in the human body. Therefore, although their concentrations were low, HCH is clearly present in most soil samples.

Compared with other regions in the world, the ΣDDT concentrations obtained in Hanoi are comparable to those in soil samples of Shanghai, China (18–142 ng g^{-1}) and lower than those in Tasmania, New Zealand (30–34,500 ng g^{-1}) or Beijing, China (0.77–2,178 ng g^{-1}; Nakata et al., 2005; Zhu et al., 2005; Gaw et al., 2006). Meanwhile, the ΣHCH concentrations obtained in Hanoi are lower than those in soil samples from Beijing, China (1.36–56.61 ng g^{-1}) or Tanzania (<0.1–59 ng g^{-1}) and higher than the residue levels found in Shanghai (<0.03–2.4 ng g^{-1}; Kishimba et al., 2004; Nakata et al., 2005; Zhu et al., 2005).

Besides contamination of the soil, DDT and HCH have also found ways to penetrate the human body and other environments in Hanoi. According to Nhan et al. (2001), the ΣDDT and ΣHCH concentrations in sediments from canals in the downtown area and the suburbs of Hanoi city in August 1997 ranged from 7 to 80 ng g^{-1} and 0.1 to 3.1 ng g^{-1} dry weight, respectively. Hung et al. (2002) detected ΣDDT and ΣHCH on the surface of four lakes in the centre of Hanoi, as well as six irrigation canals, and two nearby rivers. It has been reported that the mean ΣDDT and ΣHCH concentrations in the lakes in August 1999 were 5.07 ± 6.88 ng l^{-1} and 31.7 ± 60.4 ng l^{-1}, respectively. In addition, Minh et al. (2004) found that the mean ΣDDT and β-HCH concentrations in 42 human breast-milk samples in Hanoi were 2,100 and 58 ng g^{-1} lipid weight, respectively. These results, together with our study, highlight the widespread contamination by DDT and HCH in Hanoi.

Composition differences of HCH isomers or DDT metabolites in the environment could indicate different contamination sources. DDT was imported and used in Vietnam from 1957 to 1994. It was banned in Vietnam due to its high toxicity and long-term residue in the environment (Hung et al., 2002). In general, technical DDT contains 65–80% of *p,p′*-DDT, 15–21% of *o,p′*-DDT, up to 4% of *p,p′*-DDD, and up to 1.5% of 1-(*p*-chlorophenyl)-2,2,2-trichloro ethanol (ATSDR, 2002). The mean percentages of DDT and its metabolites in the soil samples from Hanoi followed the order *p,p′*-DDE (54.4%) > *p,p′*-DDD (25.5%) > *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 soil conditions, the active oxidative transformation of *p,p′*-DDT to *p,p′*-DDE was facilitated and created this order. 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 various places in India. With regard to DDT metabolites, the ratio of (*p,p′*-DDE + *p,p′*-DDD)/ΣDDT in the soil samples of Hanoi ranged between 0.75 and 0.99 with a mean of 0.79, which indicates that significant degradation of DDT had occurred. This is also a strong indication that no recent input of DDT in Hanoi has occurred.

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

Location	α-HCH	β-HCH	γ-HCH	δ-HCH	ΣHCH	p,p′-DDE	p,p′-DDD	p,p′-DDT	ΣDDT
A. Agricultural areas									
SocSon 1 [(a)]									
C1	2.66	2.96	0.65	0.29	6.56	98.65	45.44	17.75	161.84
C2	2.88	3.69	0.79	0.29	7.65	93.58	45.75	24.42	163.75
C3	3.09	3.49	0.78	0.39	7.75	53.69	25.24	23.32	102.25
C4	4.08	4.26	1.07	0.98	10.39	54.64	27.43	24.19	106.26
C5	3.86	4.26	1.08	1.18	10.38	93.16	44.67	24.93	162.76
C6	3.98	4.19	0.97	0.63	9.77	49.94	25.97	22.75	98.66
C7	3.67	4.08	0.95	0.46	9.16	50.92	23.42	22.38	96.72
C8	2.57	2.25	0.96	0.69	6.47	48.85	23.48	21.92	94.25
DongAnh 1									
C9	2.06	2.35	0.56	0.59	5.56	43.68	22.68	19.9	86.26
C10	2.58	2.97	0.67	0.15	6.37	46.48	24.86	21.42	92.76
C11	2.26	2.98	0.76	0.56	6.56	49.78	24.39	23.49	97.66
C12	2.66	3.67	0.76	0.57	7.66	47.79	25.87	22.06	95.72
C13	1.68	2.66	0.56	0.16	5.06	33.69	16.44	14.12	64.25
C14	2.45	2.76	0.68	0.49	6.38	32.86	17.97	12.99	63.82
C15	2.26	2.98	0.69	0.46	6.39	33.14	15.43	13.7	62.27
GiaLam 1									
C16	3.19	3.96	0.87	0.68	8.69	47.92	21.44	18.98	88.34
C17	2.36	2.68	0.78	0.47	6.29	43.15	21.44	18.06	82.65
C18	2.26	2.48	0.56	0.37	5.67	35.58	16.38	15.47	67.43
Hanoi centre 1									
C19	2.66	2.48	0.86	0.56	6.56	24.72	13.15	5.38	43.25
C20	2.68	2.96	0.66	0.59	6.89	14.19	8.12	0.05	22.36
C21	1.48	2.95	0.28	0.25	4.96	28.17	13.12	5.15	46.44
TuLiem 1									
C22	5.86	6.68	1.46	0.56	14.56	83.75	43.56	40.96	168.27
C23	6.07	6.19	1.46	0.96	14.68	78.92	45.29	40.17	164.38
C24	3.06	3.48	0.76	0.26	7.56	35.97	17.36	14.99	68.32
C25	3.16	3.39	0.75	0.09	7.39	33.78	14.73	12.84	61.35
C26	3.57	3.86	0.86	0.27	8.56	32.23	15.96	14.28	62.47
C27	3.67	3.79	0.86	0.36	8.68	29.94	15.74	13.95	59.63
C28	3.49	3.98	0.84	0.18	8.49	31.32	14.19	12.83	58.34
ThanhTri 1									
C29	<0.05	<0.05	<0.05	<0.05	<0.05	<0.02	<0.02	<0.02	<0.02
C30	8.56	9.28	1.86	0.87	20.57	97.54	49.36	24.93	171.83
C31	3.15	3.38	0.76	0.08	7.37	42.92	16.59	11.85	71.36
B. Industrial and urban areas									
SocSon 2 [(b)]									
C32	2.37	2.39	0.57	0.26	5.59	36.82	17.88	9.02	63.72
C33	2.36	2.06	0.58	0.57	5.57	36.73	17.16	13.93	67.82
C34	<0.05	<0.05	<0.05	<0.05	<0.05	<0.02	<0.02	<0.02	<0.02
DongAnh 2									
C35	2.26	2.36	0.58	0.16	5.36	19.43	9.63	9.18	38.24
C36	<0.05	<0.05	<0.05	<0.05	<0.05	<0.02	<0.02	<0.02	<0.02
C37	2.28	1.96	0.77	0.36	5.37	18.56	9.82	7.94	36.32
C38	<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
C39	<0.05	<0.05	<0.05	<0.05	<0.05	<0.02	<0.02	<0.02	<0.02
GiaLam 2									
C40	<0.05	<0.05	<0.05	<0.05	<0.05	<0.02	<0.02	<0.02	<0.02
C41	<0.05	<0.05	<0.05	<0.05	<0.05	<0.02	<0.02	<0.02	<0.02
C42	<0.05	<0.05	<0.05	<0.05	<0.05	<0.02	<0.02	<0.02	<0.02
C43	3.27	2.89	0.76	0.66	7.58	33.28	15.86	14.44	63.58
C44	3.17	2.86	0.77	0.96	7.76	35.19	16.83	15.45	67.47
C45	1.76	1.86	0.38	0.28	4.28	13.39	5.62	4.15	23.16
C46	1.56	1.76	0.86	0.48	4.66	13.56	4.98	3.89	22.43
Hanoi centre 2									
C47	<0.05	<0.05	<0.05	<0.05	<0.05	<0.02	<0.02	<0.02	<0.02
C48	2.36	2.08	0.77	0.58	5.79	8.32	2.54	2.32	13.18
C49	<0.05	<0.05	<0.05	<0.05	<0.05	<0.02	<0.02	<0.02	<0.02
C50	<0.05	<0.05	<0.05	<0.05	<0.05	<0.02	<0.02	<0.02	<0.02
C51	2.19	1.79	0.59	0.29	4.86	13.34	5.54	4.74	23.62
C52	<0.05	<0.05	<0.05	<0.05	<0.05	<0.02	<0.02	<0.02	<0.02
C53	1.88	1.96	0.57	0.47	4.88	13.68	5.92	5.16	24.76
TuLiem 2									
C54	2.16	2.37	0.57	0.66	5.76	17.66	7.38	7.12	32.16
C55	2.36	2.08	0.78	0.56	5.78	19.48	7.98	7.72	35.18
C56	1.98	1.96	0.56	0.36	4.86	14.84	5.88	5.62	26.34
C57	1.98	2.16	0.47	0.16	4.77	16.89	8.59	6.94	32.42
ThanhTri 2									
C58	2.36	2.08	0.76	0.46	5.66	13.44	4.74	4.39	22.57
C59	2.29	1.86	0.68	0.46	5.29	12.98	4.92	4.39	22.29
C60	<0.05	<0.05	<0.05	<0.05	<0.05	<0.02	<0.02	<0.02	<0.02

(a) SocSon 1: agricultural areas of SocSon; (b) SocSon 2: industrial and urban areas of SocSon

Technical HCH and lindane (>99% γ-HCH) have been officially banned since 1994 in Vietnam. Typical technical HCH contains 55–80% α-HCH, 5–14% β-HCH, 8–15% γ-HCH and 2–16% δ-HCH (Lee et al., 2001). The mean percentages of HCH isomers in most of our soil samples from Hanoi followed the order β-HCH (42.8%) > α-HCH (39.7%) > γ-HCH (10.9%) > δ-HCH (6.6%). Among the isomers, β-HCH has the lowest water solubility and vapor pressure, and is the most stable and resistant to microbial degradation. One should also consider the isomerization of α- to β-HCH and of γ- via α- to the more stable β-HCH, which is energetically favorable 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 indicate the use of technical HCH. The α-HCH/γ-HCH ratio in areas where lindane has typically been used ranges from 0.2 to 1, compared to 4–15 for technical HCH (McConnell et al., 1993). Here, the mean ratio of α-HCH/γ-HCH in the analyzed soil samples was 3.7. According to Nhan et al. (2001), the proportion of β-HCH, α-HCH and γ-HCH in sediments collected from 12 locations in canals in the downtown area and the suburbs of Hanoi city are similar to those of the technical HCH mixture. This observation also corresponds with the results of our study, that technical HCH was the main source of HCH contamination in surface soil from Hanoi.

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