

Pesticide residues in soils, sediments, and vegetables in the Red River Delta, northern Vietnam

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Abstract This study assessed pesticide residues in soils, sediments, and vegetables in the Xuan Khe and Hop Ly communes located along the Chau Giang River in the Red River Delta, northern Vietnam. Samples were collected from agricultural areas within and outside of embankments built to prevent flooding. In Xuan Khe, the soils outside of the embankment were more clayey with higher organic matter contents compared with the inside, due to selective deposition during river flooding. Many of the soils contained significant amounts of pesticides including dichlorodiphenyltrichloroethane (DDT), dicofol, isoprothiolane, and metalaxyl although their levels were below the maximum allowable concentration set by the Vietnamese gov-

ernment. The spectrum of DDT derivatives found suggested that the source of DDTs was not contaminated dicofol. Soils in Hop Ly resembled soils in Xuan Khe but were relatively sandy; one field showed appreciable contents of DDT derivatives. The ratios of (*p,p'*-dichlorodiphenyldichloroethylene + *p,p'*-dichlorodiphenyldichloroethane)/ \sum DDT in the surface and subsurface soils in Hop Ly were 0.34 and 0.57, suggesting that the DDTs originated from recent application. Pesticide residues in soils were not likely to translocate into vegetable crops, except for metalaxyl. High concentrations of cypermethrins in kohlrabi leaves could be ascribed to foliar deposition.

Keywords Pesticide residues · DDTs · Red River Delta · Flooding · Soils · Vegetables

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Introduction

In Asian developing countries, much attention has been paid to pollution by pesticide residues in agricultural environments since proper regulations were implemented and the phase-out of highly toxic pesticides commenced in the 1980s and 1990s (Thao et al. 1993; Gong et al. 2004; Kim and Smith 2001; Bishnu et al. 2008). Integrated Pest Management (IPM) programs were implemented by Food and Agriculture

Organization (FAO) and other organizations in the 1990s (Pontius et al. 2000; Winarto 2004). In Vietnam, these IPM programs improved the knowledge of local farmers about pesticide use significantly, resulting in the reduction of pesticide application rates and a plunge in the total consumption of pesticides in this country (Berg 2001; FAOSTAT 2008). However, few studies have been conducted on the residues of currently used pesticides. Khanh et al. (2006) reported that the overuse of pesticides for weeding is still a serious problem in Vietnam, causing environmental pollution, unsafe agricultural products, and human health hazards. Therefore, the fate of pesticides remaining in the environment should be monitored to improve the safety of agricultural products.

In general, soils in river deltas are extraordinarily fertile, resulting in extensive agricultural activities. In deltas, the soil texture can be expected to change from coarser to finer with increasing distance from the river due to translocation and sedimentation during flooding (Leet and Judson 1960). Several surveys of residual pesticides have been conducted in the Red River Delta (Nhan et al. 1998; Toan et al. 2007) and Mekong

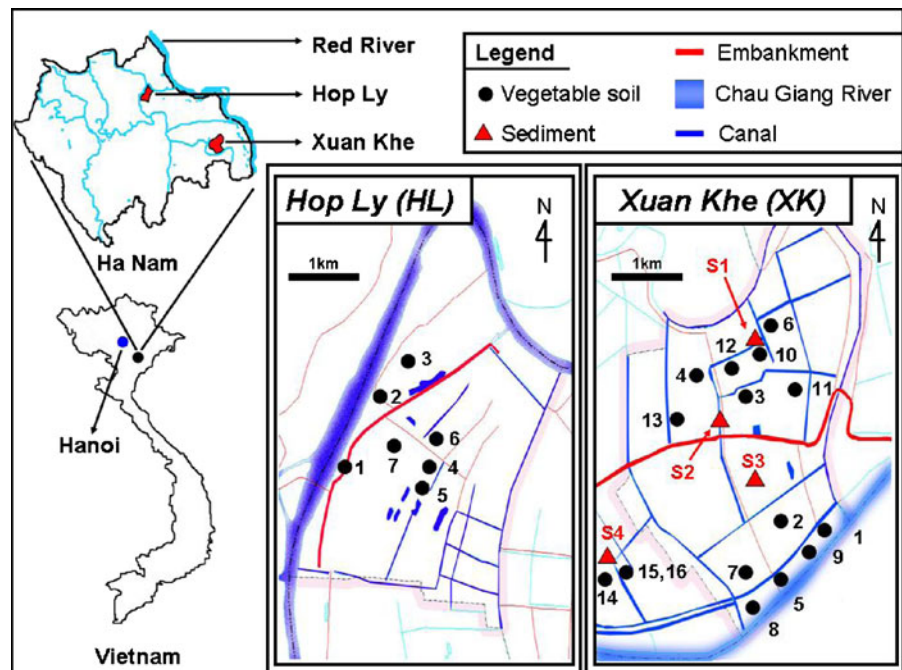
River Delta (Minh et al. 2007b). Although these researches revealed that organochlorine pesticides were present in river sediments and in agricultural and industrial soils, they did not compare the pesticide status of farm lands in terms of the soil texture and its dependence on the distance from rivers. In this study, we focused on pesticide residues in agricultural soils of the Red River Delta, the second largest agricultural area in Vietnam. The aims of this study are (1) to evaluate the pesticide status of soils on farm lands within and outside the flooding area of the Red River and (2) to understand vertical and horizontal movements of pesticides to better understand their fate in this agricultural environment.

Materials and methods

Study area

This study was conducted in the Xuan Khe (XK; 20°31'474" N, 106°7'319" E) and Hop Ly (HL; 20°36'678" N, 105°59'311" E) communes in the Ha Nam Province, northern Vietnam, located along the Chau Giang River, one of the tributaries of the

Fig. 1 The location of sampling sites Hop Ly and Xuan Khe, Vietnam



Red River (Fig. 1). The surroundings of the Red River and its tributaries are flooded annually in the rainy season of every year. Elevated embankments were constructed in the two communes in the late 1950s to prevent flood damages to residential and agricultural areas. The embankments divide the communal areas into a flooded (F) area and an area rarely affected by floods (nonflooded (NF) area). The study region is characterized by a monsoonal climate with distinct summer (May to September) and winter (mid-November to mid-March) seasons and two transitional seasons including spring (mid-March to the end of April) and autumn (October to mid-November). The annual average temperature ranges from 23°C to 24°C. The average precipitation is approximately 1,900 mm (Ha Nam People's Committee 2004). Agricultural activities are based on the rotation of lowland rice and vegetable cultivation. Rice plants are cropped twice a year from February to June and from July to October, followed by vegetable cropping from the end of October to late February. Common vegetables planted in the area are cabbage (*Brassica oleracea* L. var. *capitata*), corn (*Zea mays* L.), cucumber (*Cucumis sativus*), kohlrabi (*B. oleracea* var. *gongyloides*), and soybean (*Glycine max*). Farmers usually apply insecticides to vegetables when harmful insects or disease symptoms occur. Generally, insecticides are applied more intensively to crops for human consumption such as cabbage and cucumber than to corn which is used as livestock feed.

Sampling

Field surveys and sample collection were conducted in November 2006 and November 2007. In 2006, soil samples were collected from several agricultural fields in XK and HL to study soil characteristics and pesticide residue contents and the possible effects of the embankments. Then, in 2007, samples of soils, sediments, and vegetables were collected from XK to understand pesticide movements. Soil samples were collected from nine and seven fields in the F and NF areas, respectively, of Xuan Khe and from three and four fields in the F and NF areas, respectively, of Hop Ly (Table 1). Each field was divided equally

into four quarters and surface (0–5 cm) and sub-surface (20–25 cm) soil samples were collected at the centers of the quarters. Immediately after the four samples of equal weight were collected, they were thoroughly mixed to obtain one composite sample. Soil profiles were characterized at XK-F8 and XK-NF10. In addition, sediments were sampled using an Ekman dredge from irrigation canals and the river. Soil and sediment samples were stored in amber glass bottles. As shown in Table 1, vegetable samples were collected from 12 selected fields. Vegetables (eight cabbages, 20 ears of corn, 50 cucumbers, eight kohlrabi, and 100 soybean pods with beans) were harvested near the center of the quarters, and equal portions of each subsample were taken to obtain approximately 1 kg of representative samples from each field. The samples were wrapped in Teflon sheets and immediately frozen in a refrigerator at -30°C . Then, all samples were exported to Japan while being kept frozen at -30°C . In Japan, the soil samples were air-dried in a room and restored at -30°C .

Physico-chemical properties of soils and sediments

Soil particle size distributions were determined with a pipette method (Gee and Bauder 1986). The electric conductivity (EC) and pH (H_2O) were determined using an EC and pH meter (pH/COND METER D-54, Horiba, Kyoto, Japan) with a soil-to-water ratio of 1:5 (w/v). Exchangeable bases (Na^+ , K^+ , Mg^{2+} , Ca^{2+}) were extracted with 1 mol L^{-1} ammonium acetate at pH 7.0, and the contents were determined using an atomic absorption spectrometer (AA-6800 Shimadzu, Kyoto, Japan). After removing excess NH_4^+ , the soil was extracted with 100 g L^{-1} NaCl solution, and the supernatant was used to determine the cation exchange capacity (CEC) with the Kjeldahl distillation and titration method (Rhoades 1982). The content of total carbon was analyzed by a CN analyzer (Microcorder JM10, J Science Lab, Kyoto, Japan). The total carbon value was converted to organic matter contents by multiplying the value by 1.724 (Nelson and Sommers 1982).

Table 1 List of soil, vegetable, and sediment samples collected from Xuan Khe and Hop Ly in the Ha Nam Province, northern Vietnam

Locations	Crops	Field size (a)	Soils		Vegetables
			2006	2007	
Xuan Khe					
Flooded area (upland fields)					
XK-F1	Corn	72.0	Y		Y
XK-F2	Kohlrabi	1.35	Y		Y
XK-F5	Corn	72.0	Y		Y
XK-F7	Cabbage	0.60	Y		
XK-F8	Corn	2.38	Y		Y
XK-F9	Kohlrabi	0.98		Y	Y
XK-F14	Cucumber	0.30		Y	Y
XK-F15	Cabbage	1.50		Y	Y
XK-F16	Soybean	2.00		Y	Y
Sediments					
XK-FS3				Y	
XK-FS4				Y	
Nonflooded area (upland fields)					
XK-NF3	Soybean	3.12	Y		
XK-NF4	Cucumber	1.98	Y		
XK-NF6	Corn	3.42	Y		
XK-NF10	Corn	3.20		Y	Y
XK-NF11	Kohlrabi	0.20		Y	Y
XK-NF12	Soybean	0.60		Y	Y
XK-NF13	Cucumber	3.12		Y	Y
Sediments					
XK-NFS1				Y	
XK-NFS2				Y	
Hop Ly					
Flooded area (upland fields)					
HL-F1	Kohlrabi	1.68	Y		
HL-F2	Lettuce	2.00	Y		
HL-F3	Corn	4.00	Y		
Nonflooded area (upland fields)					
HL-NF4	Cabbage	8.60	Y		
HL-NF5	Corn	2.40	Y		
HL-NF6	Lettuce	1.00	Y		
HL-NF7	Corn	3.84	Y		

This survey was conducted in 2006 and 2007. In the two communes Xuan Khe and Hop Ly, only soil samples were collected in 2006. In 2007, soil, sediment, and vegetable samples were collected only in XK *F* flooded area type, *NF* nonflooded area type, *XK* Xuan Khe, *HL* Hop Ly, *Y* year when the soil and vegetable samples were collected in XK and HL

Simultaneous analysis of pesticides

Pesticides in soil, sediment, and vegetable samples were screened following the method by Yabuta et al. (2002) with some modifications. In the case of soil and sediment samples, 10-g air-dried samples were extracted twice with 30 and 20 mL acetonitrile by shaking for 1 h. The solution was filtered using a glass filter (Glass microfiber filters GF/B, Whatman, Maidstone, England) and 16 mL water was added. Then, the extract was passed through a C18 cartridge. After adding 7 mL 2 mol L⁻¹ phosphate buffer saturated with

NaCl (pH 7.5), the extract was separated in a separatory funnel containing 8.0 g NaCl. The acetonitrile layer obtained was concentrated using a rotary evaporator and dried under a gentle stream of nitrogen. The dried extract was loaded with 2 mL of acetone/hexane (1:1) onto a cartridge packed with 0.5 g graphite carbon over 0.5 g of primary/secondary amine (PSA). The cartridge was eluted with 20 mL acetone/hexane (1:1) followed by 10 mL toluene. Fifty microliters of *n*-decane was added to the eluted extract to avoid vaporization of pesticides during the concentration process. The extract was con-

concentrated and dried under a stream of nitrogen. The final volume was adjusted to 2 mL with acetone/hexane (1:1). One hundred microliters of a standard mixture (internal standards mix 2, Hayashi Pure Chemical, Osaka, Japan) was added to the final extract as an internal standard prior to gas chromatography–mass spectrometry (GC–MS) analysis. The composition of the standard mixture was naphthalene-d8, acenaphthene-d10, phenanthrene-d10, fluoranthene-d10, chrysene-d12, and perylene-d12.

One kilogram of the collected vegetables with skins was homogenized using a home mixer. Ten grams of the previously homogenized vegetables was homogenized with 30 mL acetonitrile using a homogenizer (IKA ULTRA-TURRAX T25 digital, Staufen, Germany). The homogenate was filtered using a glass filter, and 7 mL water was added before passing the extract through a C18 cartridge. The procedure described above for soil samples was employed for subsequent steps, except for two details. First, for the elution of the graphite carbon and PSA cartridge, 20 mL of acetone/hexane (2:8) followed by 10 mL of toluene were applied. Second, the amount of PSA in the cartridge was increased to 1 g for cabbage, corn, and kohlrabi, due to remove impurities from the extracts for GC–MS analysis.

We used the GC–MS database “Compound Composer Database Software for Simultaneous Analysis” (Shimadzu, Kyoto, Japan) for automatic identification and semiquantification of pesticides. Based on the requirements for this database, a Shimadzu QP-2010 GC–MS (Shimadzu, Kyoto, Japan) with a J&W DB-5ms capillary column (Agilent Technologies, San Jose, CA, USA) was used. Prior to a series of analyses, an *n*-alkane (*n*-C₉H₂₀ to *n*-C₃₃H₆₈) mixture (Hayashi Pure Chemical, Osaka, Japan) was analyzed to adjust the retention times of registered pesticides. Pesticides identified in the samples were semiquantified with an internal standard method.

Quantification of DDTs

In this paper, dichlorodiphenyltrichloroethanes (DDTs) mean DDT and its metabolites including *p,p'*-DDT, *o,p'*-DDT, *p,p'*-dichlorodiphenyldichloroethylene (DDE), *p,p'*-

dichlorodiphenyldichloroethane (DDD), and *o,p'*-DDD. \sum DDT represents the sum of *p,p'*-isomers of DDT, DDE, and DDD. DDTs were extracted and quantified with the method reported by the Water Quality Conservation Bureau, The Japanese Environmental Agency (2000). Briefly, 20 g of air-dried soils was shaken twice with 50 mL acetone and filtered. The extracts were dissolved in 500 mL of a 50-g L⁻¹ NaCl solution. DDTs were extracted from the mixture with 50 mL hexane. The hexane extraction procedure was repeated three times. Sodium sulfate was added to the hexane extracts. After concentration with a rotary evaporator under a stream of nitrogen, the extracts were transferred to a cartridge packed with graphite carbon (0.5 g), florizil (1 g), and PSA (0.5 g), followed by elution with 35 mL acetone/hexane (85:15) and 30 mL acetone/hexane (1:1). The extracts were dried with a rotary evaporator under a nitrogen stream. The final volume of the solution was adjusted to 1 mL with hexane prior to GC–MS analysis in selected ion monitoring (SIM) mode. Recovery rates of DDTs were determined by adding DDTs standards (ACCUS standards, New Heaven, CT, USA) to the XK-F2 sample which did not contain DDTs. The recovery rates were 112%, 109%, 119%, 110%, and 135% for *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDT, and *p,p'*-DDT, respectively.

Quality control

Simultaneous analysis of pesticides

To ensure that the various pesticides could be analyzed by the analytical method for simultaneous analysis of pesticides, a standard solution containing 57 pesticides (Pesticide standard solution 32; Kanto Chemical, Tokyo, Japan) was added to representatives of each sample type to examine the recovery rates. To select the representative samples, first all soil and vegetable samples were extracted using the procedure for simultaneous analysis of pesticides described above, and pesticide residues in the samples were quantified using the SIM mode of the GC–MS with an external standard method. Then, samples which did not contain any of the pesticides were identified, and a

Table 2 The detection limit (nanograms per gram) and recovery rate (percent) of DDTs

DDTs	Detection limit (ng g ⁻¹) ^a	Recovery rate (%)
<i>p,p'</i> -DDE	0.03	112
<i>o,p'</i> -DDD	0.05	109
<i>p,p'</i> -DDD	0.16	119
<i>o,p'</i> -DDT	0.13	110
<i>p,p'</i> -DDT	0.30	135

^aDetection limits of the each DDT were calculated as three times the signal-to-noise ratio

representative sample from each sample type was chosen for examination of the recovery rates (soil: XK-F2 0–5 cm, vegetable: cabbage, XK-F15; corn, XK-F1; cucumber, XK-NF13; kohlrabi tuber, XK-F2; soybean, XK-NF12). Recovery rates were determined by adding the 57 pesticides to the samples, extracting by the procedure, and quantifying using the SIM mode of the GC–MS. Satisfactory recovery rates (50% to 150%) were obtained for 53, 46, 42, 44, 25, and 43 of the 57 pesticides added to samples of the soil, cabbage, corn, cucumber, kohlrabi tuber, and soybean, respectively.

Analysis of DDTs

For quality assurance and quality control of the analysis of DDTs, the procedural blanks and matrixes spiked with the standard solution were

analyzed. None of the target compounds were detected in the procedural blanks. Since XK-F2 did not contain any DDTs when extracted and analyzed by the methods described, it was selected and spiked with the standard solution of the DDTs for a recovery study. The spiked concentration levels of DDTs for the recovery study were 100 ng g⁻¹. The recovery rates of the DDTs spiked to the soil ranged from 109% to 135% (Table 2). The limits of detection were described as three times that of the signal-to-noise ratio. The detection limit was 0.03 to 0.3 ng g⁻¹ (Table 2).

Statistical analysis

Soil physicochemical properties were compared between F and NF areas by Tukey's multiple comparison, using the SPSS software package (Release 13.0 for Windows; SPSS Inc.).

Results

Physico-chemical properties of soils and sediments

Based on the US Department of Agriculture classification system, the soils in the XK-NF area

Table 3 General physicochemical properties of the soils

Location	pH (H ₂ O)	EC (mS m ⁻¹)	OM (g kg ⁻¹)	Exchangeable bases				CEC	Clay	Silt	Sand
				Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺				
cmol _c kg ⁻¹											
%											
Surface											
XK-F (<i>n</i> = 7) ^a	7.21 A	39.4 A	11.3 B	0.25 B	0.34 A	14.5 A	2.20 AB	10.2 B	19 B	32 A	48 A
XK-NF (<i>n</i> = 7)	5.94 B	46.9 A	21.6 A	0.51 A	0.29 A	11.0 AB	2.87 A	14.9 A	43 A	40 A	16 B
HL-F (<i>n</i> = 4)	6.69 A	26.4 A	6.8 B	0.19 B	0.11 A	7.7 B	1.54 B	6.43 B	7 B	25 A	68 A
HL-NF (<i>n</i> = 3)	6.10 A	18.3 A	7.4 B	0.19 B	0.12 A	6.9 B	1.38 B	7.86 B	13 B	35 A	51 A
Subsurface											
XK-F (<i>n</i> = 7)	7.32 a	14.2 a	7.7 b	0.22 b	0.15 ab	13.6 a	1.81 b	8.72 b	18 b	30 a	51 a
XK-NF (<i>n</i> = 7)	6.58 a	26.4 a	14.2 a	0.49 a	0.20 a	9.8 a	3.07 a	13.7 a	46 a	40 a	14 b
HL-F (<i>n</i> = 4v)	8.10 a	10.6 a	4.0 b	0.17 b	0.06 bc	11.3 a	1.34 b	7.13 b	12 b	27 a	61 a
HL-NF (<i>n</i> = 3)	7.42 a	10.1 a	3.7 b	0.18 b	0.09 b	14.6 a	1.67 b	9.08 ab	21 b	40 a	39 ab

Average values followed by the same capital letter are not significantly different at the 5% level (surface soils) and neither are those followed by the same small letter (subsurface soil), as determined by Tukey's method

OM organic matter content

^aXK-F1 and XK-F5 were omitted from the data because the composite sample may not be representative of the field due to the large field size (see Table 1)

Table 4 General physicochemical properties of sediments collected in Xuan Khe

Location	pH (H ₂ O)	EC (mS m ⁻¹)	OM (g kg ⁻¹)	Exchangeable bases				CEC	Clay %	Silt	Sand
				Na ⁺ cmol _c kg ⁻¹	K ⁺	Ca ²⁺	Mg ²⁺				
Sediment											
XK-F-SD (<i>n</i> = 2)	6.96	36.0	38.1	0.22	0.42	15.3	2.16	13.2	29	36	35
XK-NF-SD (<i>n</i> = 2)	6.08	56.3	45.5	0.31	0.52	11.7	2.38	15.0	40	37	23

SD sediment samples, *OM* organic matter content

were classified as Vertic Ustorthents while those in the XK-F area were Typic Udipsamments (Soil Survey Staff 2006). Although soil pits were not surveyed in HL, the soils in the HL-F and HL-NF areas showed similar properties as those in XK-F. Therefore, they could be tentatively classified as Typic Udipsamments or its relatives. Generally, the clay and organic matter contents of the soils in XK were higher than those in HL (Table 3). This trend was most pronounced in the subsurface soils of the XK-F and HL-F areas. Differences in the amount of exchangeable bases were insignificant between XK and HL.

In XK, the clay and organic matter contents of the NF soils were significantly higher than in the F area. On the other hand, the amounts of exchangeable bases were not significantly different between the F and NF area, except for Mg²⁺ in the subsurface soils and Na⁺ in the surface and subsurface soils. Sediments in the NF area also showed increased clay and organic matter contents but similar amounts of exchangeable bases (Table 4).

In HL, there was no significant difference in the clay and organic matter contents between the F and NF areas although values tended to

Table 5 Frequency of fields in which pesticides were detected

	Total number of fields	Number of fields with pesticides ^b	Percentage of fields with pesticides (%) ^c
Xuan Khe			
Flooded area ^a			
Surface	7	2	29
Subsurface		1	14
Sediment	2	0	
Nonflooded area			
Surface	7	6	86
Subsurface		4	57
Sediment	2	1	
Hop Ly			
Flooded area			
Surface	3	1	33
Subsurface		0	0
Nonflooded area			
Surface	4	1	25
Subsurface		1	25

XK Xuan Khe, *HL* Hop Ly

^aXK-F1 and XK-F5 were omitted from the data because the composite sample may not be representative of the field due to the large field size (see Table 1)

^bFields with pesticides indicates fields with any pesticides detected by simultaneous analysis of pesticides in the soils

^cPercentage of fields with pesticides was calculated by (number of fields with pesticides/total number of fields) × 100

be higher in the NF area except for the organic matter contents in the subsurface soils. The amounts of exchangeable bases were not significantly different between the F and NF areas.

Analysis of pesticide residues in soils, sediments, and vegetables

The frequency of fields where at least one pesticide was detected is shown in Table 5. It is evident that the fields in XK-NF were highly affected by

pesticide residues, compared with the other areas. In the F and NF areas of HL, pesticide residues were detected only in one field each.

More detailed information on the pesticides detected are given in Table 6. In the NF area of XK, DDTs were found. However, semiquantitative analysis indicated that their concentrations were lower than 5.0 and 5.3 ng g⁻¹ in the surface and subsurface soils, respectively. Isoprothiolane, metalaxyl, dicofol, and cypermethrins were also detected. Isoprothiolane was found both in the surface and subsurface soils of XK-NF3, XK-

Table 6 Pesticide residues in soils and sediments collected in Xuan Khe and Hop Ly

Sites	Surface layer (0–5 cm)			Subsurface layer (20–25 cm)	
	Crop	Pesticides	Concentration (ng g ⁻¹)	Pesticides	Concentration (ng g ⁻¹)
Xuan Khe					
Flooded area (upland fields)					
XK-F7	Cabbage	Fenobucarb	0.4		
		Chlorothalonil	36.7		
XK-F14	Cucumber	Metalaxyl	9.8	Isoprothiolane	3.5
Nonflooded area (upland fields)					
XK-NF3	Soybean	Dicofol	5.6	Dicofol	16.0
		Isoprothiolane	7.4	Isoprothiolane	8.9
		<i>p,p'</i> -DDE	1.2	<i>p,p'</i> -DDE	3.2
		<i>p,p'</i> -DDD	0.2	<i>p,p'</i> -DDD	2.2
XK-NF4	Cucumber	Metalaxyl	55.0	Metalaxyl	2.7
		Isoprothiolane	9.6	Isoprothiolane	16.6
		Cypermethrins ^a	121.9	<i>p,p'</i> -DDE	1.4
		<i>p,p'</i> -DDE	0.7		
XK-NF6	Corn	<i>p,p'</i> -DDE	0.3		
XK-NF11	Kohrlabi	Isoprothiolane	7.6		
XK-NF12	Soybean	Dicofol	6.9	Dicofol	7.3
		<i>p,p'</i> -DDE	3.6	<i>p,p'</i> -DDE	2.2
				<i>p,p'</i> -DDD	3.1
XK-NF13	Cucumber	Metalaxyl	5.9	Isoprothiolane	34.5
		Isoprothiolane	10.6		
Sediments					
XK-NFS3		Isoprothiolane	6.6		
Hop Ly					
Flooded area (upland fields)					
HL-F3	Corn	DDVP	4.8		
		Fenobucarb	0.8		
		Fenitrothion (MEP)	31.4		
Nonflooded area (upland fields)					
HL-NF6	Lettuce	<i>p,p'</i> -DDE	3.4	<i>p,p'</i> -DDE	1.7
		<i>p,p'</i> -DDD	1.6		

Pesticide residues were not detected in any of the sites omitted from this table

XK Xuan Khe, HL Hop Ly, F flooded area, NF nonflooded area

^aValues for cypermethrins are the sums for cypermethrin 1 to 4

Table 7 Pesticide residues in vegetables collected in Xuan Khe

Location	Sample type	Pesticides	Concentration (ng g ⁻¹)
Flooded area			
XK-F2	Kohlrabi (tuber)	Cypermethrins ^a	42.5
	Kohlrabi (leaf)	Cypermethrins	2,523
XK-F9	Kohlrabi (tuber)	Cypermethrins	11.1
	Kohlrabi (leaf)	Cypermethrins	2,280
XK-F14	Cucumber	Metalaxyl	54.5
XK-F16	Soybean (pod)	Cypermethrins	230
Nonflooded area			
XK-NF13	Cucumber	Metalaxyl	31.3

No pesticide residues were detected in corn in XK-F-1, XK-F-5, XK-F-8, and XK-NF-10, cabbage in XK-F-15, kohlrabi (tuber and leaf) in XK-NF-11, and soybean (bean and pod) in XK-NF-12

XK-F Xuan Khe flooded area, XK-NF Xuan Khe nonflooded area

^aValues for cypermethrins are the sums for cypermethrin 1 to 4

NF4, and XK-NF13; higher concentrations were present in the subsurface samples. Dicofol detected in XK-NF3 and XK-NF12 showed the same trend. In contrast, the concentrations of metalaxyl in the surface soils of XK-NF4, XK-NF13, and XK-NF14 were higher than in the subsurface soils while cypermethrins (cypermethrins 1 to 4) were detected at a high concentration in the surface soil of XK-NF4. In XK-F14, metalaxyl was detected in the surface soil while isoprothiolane was present in the subsurface soil. Chlorothalonil and fenobucarb were detected in XK-F7 (Table 6).

The sediment sample XK-NFS3 taken from a canal in the NF area contained isoprothiolane. No pesticides were detected in sediments collected in the F area. In HL, 2,2-dichlorovinyl dimethyl phosphate (DDVP), fenobucarb, and fenitrothion

were found only in the surface soils of HL-F3, and DDTs were detected only in the NF area.

In the vegetable samples collected in XK, pesticides were detected at a higher frequency in the F area than in the NF area, in contrast to the situation in soils (Table 7). Kohlrabis at XK-F2 and XK-F9 showed high concentrations of cypermethrins with relatively low levels in the tubers (Table 7). Cypermethrins were also detected in soybean pods at XK-F16 while metalaxyl was found in cucumbers at XK-F14 and XK-NF13.

Quantification of DDTs

Based on the results of the simultaneous analysis of multiple pesticides, DDTs were quantified in the soil samples from the XK-NF and HL-NF

Table 8 DDT and its metabolites in soils

Location	Concentration (ng g ⁻¹)					
	<i>p,p'</i> -DDE	<i>o,p'</i> -DDD	<i>p,p'</i> -DDD	<i>o,p'</i> -DDT	<i>p,p'</i> -DDT	DDTs
Xuan Khe						
XK-NF3 surface	3.84	0.71	3.59	n.d.	n.d.	8.14
XK-NF3 subsurface	4.96	n.d.	5.61	n.d.	n.d.	10.57
XK-NF4 surface	2.12	n.d.	n.d.	n.d.	n.d.	2.12
XK-NF4 subsurface	2.07	n.d.	n.d.	n.d.	n.d.	2.07
XK-NF6 surface	1.57	n.d.	2.48	n.d.	n.d.	4.05
XK-NF12 surface	5.40	1.28	3.89	n.d.	0.38	10.95
XK-NF12 subsurface	4.25	2.46	5.70	n.d.	0.54	12.95
Hop Ly						
HL-NF6 surface	7.33	n.d.	0.86	1.62	15.60	25.41
HL-NF6 subsurface	5.84	0.23	0.44	0.91	4.75	12.17

n.d. not detected

areas. In the HL-NF area, DDTs were detected only at HL-NF6, as mentioned above. The concentrations of the DDTs in the soils of the two communes ranged from 2.07 to 25.41 ng g⁻¹, with the highest value recorded in the surface soil of HL-NF6 (Table 8).

In XK, the concentrations of *p,p'*-DDE and *p,p'*-DDD exceeded those of the other DDT forms and their metabolites. In the surface soils of XK-NF3, XK-NF4, and XK-NF12, the concentration of *p,p'*-DDE were higher than that of *p,p'*-DDD. On the other hand, in the subsurface soils of XK-NF3 and XK-NF12, the concentration of *p,p'*-DDD exceeded that of *p,p'*-DDE. The concentrations of *p,p'*-DDE and *p,p'*-DDD in XK-NF3 were lower in the surface soil than in the subsurface soil, while the opposite was true in XK-NF12. It is noteworthy that *p,p'*-DDT and *o,p'*-DDD were detected only in the surface and subsurface soils of XK-NF12. Compared with the results from XK, the concentrations of *p,p'*-DDT detected in HL-NF6 were very high; *o,p'*-DDT was also found at a relatively high concentration.

Discussion

Differences in soil characteristics between the F and NF areas

In XK, the clay contents of the soils in the NF area were significantly higher than those in the F area. During flooding, fine sand, silt, and clay are carried over the flood plain away from the rivers while coarser materials are deposited within rivers and in their vicinity (Leet and Judson 1960). Therefore, the differences in the soil texture observed between the XK-F and XK-NF areas could be ascribed to the selective deposition of the sand fraction in the F area and of silt and clay in the NF area. The higher contents of organic matter and higher CEC of soils in the NF area were probably due to their clayey texture because clay particles protect soil organic matter from decomposition (Foth 1984).

In HL, higher clay and organic matter contents were found in the NF than in the F area although the differences were not statistically significant. This might be ascribed to the relative closeness of

the HL-NF area to the river compared with the situation in XK (Fig. 1).

In spite of higher clay and organic matter contents in the NF areas as compared to the F areas, the amounts of exchangeable bases tended to be similar in F and NF areas. This might be a result of the similar agricultural practices including fertilizer application in the two communes.

Pesticide residues in soils, sediments, and vegetables

In the northern mountainous region of Vietnam, Sugiura (2004) found that pesticides commonly applied to rice, tomato, kohlrabi, tea, and orange were alpha-cypermethrin, chlorothalonil, fenitrothion, and fenobucarb. In addition to these pesticides, isoprothiolane and metalaxyl were commonly used by the farmers of the communes under the survey. The Vietnamese government set the maximum allowable concentration (MAC) in soils at 500 ng g⁻¹ for cypermethrins and at 100 ng g⁻¹ for isoprothiolane and fenobucarb (TCVN 5941 1995). Cypermethrins, isoprothiolane, and fenobucarb detected in our study were below the MACs. Bishnu et al. (2008) reported that dicofol contents in tea fields ranged from below 10 to 896 ng g⁻¹ at 15 to 20 days after application, while those of cypermethrin remained below 10 ng g⁻¹. Compared to these values, the present study showed higher concentrations of cypermethrins and much lower concentrations of dicofol.

Pesticide residues occurred most frequently in the XK-NF area. Organic matter plays an important role in retaining pesticides and organic compounds in soils (Chen et al. 2005; Gong et al. 2004). Our results suggested that the clayey soils with high organic matter contents in the XK-NF area had a higher ability to retain pesticides than the sandy soils in XK-F, HL-F, and HL-NF areas, which agreed with previous reports.

Since pesticide residues were found at higher frequencies in the XK soils, additional samples of vegetables and sediments were taken in XK to understand pesticide movements. In contrast to the trends observed in the soils, kohlrabi leaves and soybean pods collected from the XK-F area contained high concentrations of cypermethrins.

Since cypermethrins had not been detected in XK-F9 and XK-F16 soil samples, foliar deposition may be the main source of cypermethrins at these locations. Plant architecture significantly affects pesticide interception. For example, Repley et al. (2003) noted that the residual levels of applied pesticides were lower on head lettuce whose architecture allowed pesticides to be deposited on all leaves. Since kohlrabi leaf blades form several layers above the tubers where they may intercept sprayed pesticides, the high concentration of cypermethrins observed was probably due to increased deposition on the plants. Compared to the high concentrations in the kohlrabi leaves, the concentrations of cypermethrins in the kohlrabi tubers, the edible part of the kohlrabi, were lower than the maximum allowable concentrations set by the Vietnamese government. Therefore, the risk of food poisoning for humans was considered to be low.

In the case of metalaxyl, there could be two ways for this compound to migrate into the cucumber, either by foliar deposition or by root uptake; this was based on the fact that it was found in the fruits as well as in the soils of the cucumber fields. On the other hand, the isoprothiolane, DDTs, and dicofol present in the soils were probably not readily available for uptake by the vegetables since the concentration of these pesticides was low compared to that of the metalaxyl in the soil, and they were not detected in the vegetables.

Pesticide profile

Isoprothiolane and metalaxyl have similar K_{oc} values of 258 ml g⁻¹ (Sudo et al. 2002) and 29–287 mg g⁻¹ (Hornsby et al. 1996), respectively. In spite of this similarity, the concentrations of isoprothiolane were higher in the surface soils than those in the subsurface soils while the opposite trend was observed for metalaxyl. This may be explained by differences in the application schedule. Isoprothiolane is frequently applied to rice plants to prevent rice blast infection during the summer season. Therefore, isoprothiolane might have gradually leached to the subsurface soils where it was detected when samples were taken in November. Isoprothiolane was also detected in

sediments collected from a canal in the XK-NF area (XK-NFS3). This supported the idea that isoprothiolane had been applied in the previous cultivation season, leached to subsurface soil layers, and subsequently moved into the canal. On the other hand, farmers apply metalaxyl to cucumber to prevent dumping off. Since our samples were collected in the harvesting season of cucumber, the pesticide still was present mainly in the surface soils.

Dicofol was detected at higher concentrations in the subsurface soils than in the surface soils at XK-NF3 and XK-NF12. Accurate data on the usage of dicofol in Vietnam is not available (Minh et al. 2006, 2007a). However, the higher concentrations of dicofol in the subsurface soils as compared to the surface layers suggested that it had been applied in a previous cultivating season.

DDT in soils

Thao et al. (1993) collected soil samples from five paddy fields near Hanoi in 1990 and reported that the summed concentrations of *p,p'*-DDE, *p,p'*-DDD, *p,p'*-DDT, and *o,p'*-DDT ranged from 0.73 to 1,300 ng g⁻¹. On the other hand, the concentrations of *p,p'*-DDE, *p,p'*-DDD, and *p,p'*-DDT ranged from <0.02 to 171.83 ng g⁻¹ in 60 surface soil samples collected in 2006 from agricultural and industrial areas in the center and suburban districts of Hanoi (Toan et al. 2007). Compared to those values, the concentration range of DDTs obtained in the present study (1.57 to 25.41 ng g⁻¹) was low and well below the MAC of 100 ng g⁻¹. These data suggest that DDTs in soils tend to decline in Vietnam, although the concentrations of DDTs are highly variable depending on the sampling location.

The concentrations of DDTs in XK-NF3 and XK-NF12 were higher in the subsurface soils than in the surface soils, which implied that a portion of the DDT applied to the surface soils was degraded as it moved downward. The concentrations of DDTs in XK-NF3 and XK-NF12 were higher in the subsurface soils than in the surface soils, which implied that the DDT applied to the surface soils was leached downward. Moreover, in the subsurface soils, the higher concentration of *p,p'*-DDD than that of *p,p'*-DDE could possibly indicate that

the anaerobic conditions of the clayey soils in XK enhanced the anaerobic degradation of DDT to DDD.

Toan et al. (2007) reported that the ratio of $(p,p'$ -DDE + p,p' -DDD)/ \sum DDT in soils collected from the greater Hanoi area ranged from 0.75 to 0.99 and suggested that significant degradation of DDT had occurred in the soils. The ratios of $(p,p'$ -DDE + p,p' -DDD)/ \sum DDT in XK-NF-13 were 0.96 and 0.95 in the surface and subsurface soils, respectively, comparable to the highest value reported by Toan et al. (2007). These high ratios indicated significant degradation of DDT and suggested no recent input of DDT in XK.

Dicofol was detected in XK-NF3 and XK-NF12 together with DDTs. Qui et al. (2005) reported that dicofol contained approximately 10% to 32% DDTs. These DDT contaminations are characterized by a high proportion of o,p' -DDT. However, we did not detect o,p' -DDT, suggesting that the DDTs we detected were not due to an application of DDT-contaminated dicofol but to previous applications of DDT.

The concentrations of DDTs were higher in HL than in XK. The ratios of $(p,p'$ -DDE + p,p' -DDD)/ \sum DDT in HL-NF6 were 0.34 and 0.57 in the surface and subsurface soils, respectively; these values were lower than those found in XK. These results may indicate a recent application of DDT in XK. The fact that the concentration of total DDTs was higher in the surface soils than in the subsurface soil supports the conclusion.

Conclusion

In this study, pesticide residues in fields of two communes in the Red River Delta were determined. Through the process of selective deposition of particles during river flooding, clayey soils with high organic matter contents were formed in the XK-NF area. These soils were found to contain more pesticides than the sandy soils in the XK-F, HL-F, and HL-NF areas. The usage of dicofol on the sites was confirmed through its residues in the soils, but the DDT that also was detected had probably not been deposited as a contamination of the dicofol applied. Although the pesticide concentrations in soils and edible

parts of vegetables were below the MAC set by the Vietnamese government, an appropriate education of farmers regarding pesticide selection and application seems necessary since our results suggest the recent usage of DDT. Therefore, it would be necessary for the Vietnamese government to take countermeasures against the application and smuggling of illegal pesticides. In addition, domestic animals fed with vegetable by-products such as kohlrabi leaves may be affected as these materials were found to contain high pesticide concentrations, raising the possibility of undesired pesticide bioaccumulation.

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