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Contamination by selected chlorinated pesticides in surface waters in Hanoi, Vietnam

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Abstract

Fifteen insecticides, which were banned in Vietnam in the period from 1990 to 1998, were chosen for the investigation of surface water samples in Hanoi and its surroundings. The investigation was focused on an area of ≈30 by 20 km. Thirty water samples, in total were analysed: 11 samples from the Red river, seven from the Duong river, four from various lakes (*West lake*, *Thuyen Quang*, *Bay Mau*, *Ba Mau*), six from irrigation canals and two samples from wells. The procedure was repeated in November 1998 and in August 1999. The results showed that the contamination of the banned pesticides was highest in the rivers and then in the irrigation canals, followed by the lakes and wells. These pesticides could hardly be determined in just two drinking water samples (wells) and their concentrations rarely exceeded detection limits (0.05–0.25 ng l^{-1}). The mean concentrations of ΣHCHs (α,β,γ,δ-HCH) and ΣDDTs (2,4′-, 4,4′-DDE; 2,4′-, 4,4′-DDD; 2,4′-, 4,4′-DDT) in the rivers were 17.2 ± 71.8 and 43.7 ± 79.9 ng l^{-1} in the dry season (DS, November 1998), 29.3 ± 117 and 56.1 ± 65.6 ng l^{-1} in the rainy season (RS, August 1999), respectively. However, the highest concentration of DDTs detected in a river sample (DS): 0.324 μg l^{-1} was much lower than their allowable limit of concentration in surface waters, which is accorded with Criteria of Vietnam (1995) (DDTs < 10 μg l^{-1}). Moreover, endrin, heptachlor, aldrin were also detected in most of water samples with considerable mean concentrations in rivers: 25.3 ± 40.5, 17.4 ± 23.8, 11.0 ± 9.02 ng l^{-1} in the DS and 18.5 ± 23.2, 19.3 ± 29.0, 12.8 ± 8.44 ng l^{-1} in the RS, respectively. Heptachlor epoxide (isomer A) and dieldrin were detected in some water samples with lowest concentrations.

Keywords: Organochlorine pesticides; Lindane; Malaria; DDT; River water contamination

1. Introduction

The use of DDT and other chlorinated hydrocarbon insecticides increased in the fifties of 20th century due to their effectiveness against a wide range of insect pests, residual activity, and relatively low mammalian toxicity. More recently the use of many of these insecticides has become limited due to their persistence in biological systems. Included in the chlorinated hydrocarbon insecticide group are DDT (dichlorodiphenyl trichloroethane), methoxychlor, aldrin, dieldrin, chlordane, toxaphene, endrin, heptachlor, and lindane (gamma isomer of benzene hexachloride (BHC)). These are trade names for closely related hydrocarbon compounds to which several chlorine atoms have been joined.

Half-lives of 9–116 years for the degradation process of these compounds could be demonstrated at a temperature of 200 °C in the soil (UBA Umweltbundesamt, 1992, 1993). The worldwide application of organochlorine pesticides is a health problem. Due to their lipophilic nature, these substances penetrate cells membrane comparatively easily (Cetinkaya, 1985). For example,

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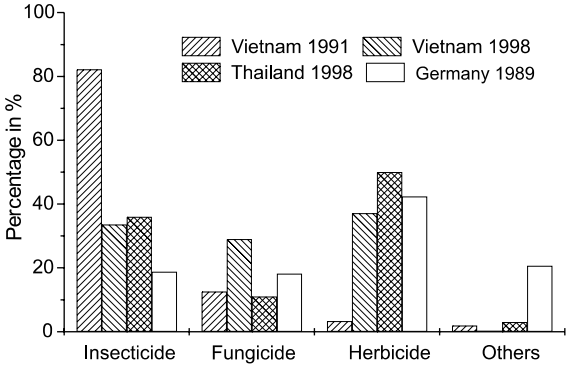

Fig. 1. A survey of the percentage distribution of authorised pesticide preparations with regard to their corresponding areas of influence in Vietnam (1991 and 1998), in Thailand (1998) (Quyen et al., 1998) and in Germany (1989) (CD Roempp, 1995).

DDT is fat soluble and is disseminated by air and water to terrestrial and aquatic ecosystems. When DDT enters a water environment, it is taken up by aquatic animals and becomes part of the food chain, accumulating and concentrating in the fat of predatory species. DDT also remains residual in upper soil layers and accumulates in many terrestrial animal species.

Vietnam has an area of 330 669 km^2 and 80% of its 77 million inhabitants work in agriculture. In 1999, Vietnam exported more than four million tons of rice and is today the second-largest rice exporter in the world. Most of the insecticides used in Vietnam are applied in agriculture (in 1991: 82%, Fig. 1), while in Germany in 1989, this rate is only 19%. In Vietnam, different pesticides were applied not only in agriculture (1992: 21 400 tons; 1997: 40 973 tons (Quyen et al., 1998), in comparison with Germany 1991: 36 937 tons (Statistisches Bundesamt, 1993)) but also in the health service, e.g. for the use of DDT against malaria/mosquito from 1957 to 1994: 24 042 tons (Table 1) (Tu and Bien, 1998; Hien, 1999). Currently, the contamination of insecticides in Vietnam is most concerned, because of their large amount used. Recently, the relative proportions of pesticides have been changed in Vietnam (insecticide: 33%, fungicide: 29%, herbicide: 37% in 1998). The amount of insecticide used was also similar in Thailand (insecticide: 36%, fungicide: 11%, herbicide: 50% in 1998), the worldwide leading country in rice export. The change in this relationship is beneficial for the environment, because of the higher toxicity of most insecticides compared with herbicides or fungicides. But insecticides were still used in large amount in other countries, including India (70%, 1998) and the Philippines (56%, 1998).

Chlorinated pesticides are still employed in some Third World countries. In Vietnam, a prohibition of these pesticides was first issued in 1993. Since then the contamination of these compounds in different environmental compartments has been studied. In Germany, even more than 25 years after being prohibited, derivatives of DDT, including DDD (1,1-dichlor-2, 2-bis(4-chlorphenyl) ethane), DDE (1,1-dichlor-2,2-bis(4-chlorphenyle) ethylene), DDA (1,1-dichlor-2, 2-bis(4-chlorphenyl) acetic acid) were detected and identified in canal waters (Duennbier et al., 1997; Heberer and Duennbier, 1999). In America (USA, Nicaragua), Europe (Germany, Russian Federation), Africa (Egypt) as well as in Asia (China), the presence of these pesticides in surface waters, sediment and suspended solids have been investigated in detail (e.g.: Castilho et al., 2000;

Table 1
Chemicals have been using for Malaria control in Vietnam (Hien, 1999)

Year	Quantity (T)	Chemical	Origin
1957–1979	14 847	DDT 30%	Former Soviet Union
1976–1980	1800	DDT 75%	WHO
1977–1983	4000	DDT 75%	The Netherlands
1981–1985	600	DDT 75%	Former Soviet Union
1984–1985	1733	DDT 75%	The Netherlands
1986	262	DDT 75%	WHO
1986–1990	800	DDT 75%	Former Soviet Union
1992	238	DDT 75%	Former Soviet Union
1993	34	DDT 75%	Former Soviet Union
1994	152	DDT 75%	Former Soviet Union
1995	24	ICON, deltamethrin, vectron	
1996	18	ICON 10 WP	Zeneca
1997	1.3	ICON 10 WP	Zeneca
1998	50	Permethrin 50 EC	Zeneca
	20	ICON 10 WP	
1999	50	Permethrin 50 EC	Zeneca
	20	ICON 10 WP	

Table 2
The recovery rates of HCH- and DDT isomers and other chlorinated pesticides through solid phase extraction process via octadecyl phase and elution with *n*-hexane (six measurements)

Compounds	Recovery rate in %	Standard deviation in %	Limit of detection in ng l^{-1}
α-HCH	82	7.3	0.5
β-HCH	76	7.6	1.25
Lindane (γ-HCH)	89	8.1	0.05
δ-HCH	87	10.4	0.5
Heptachlor	92	12.3	0.025
Aldrin	93	9.5	0.5
Heptachlorepoxide (isomer A)	87	7.8	0.5
2,4′-DDE	91	8.3	0.075
4,4′-DDE	90	7.1	0.5
Dieldrin	94	7.7	0.1
2,4′-DDD	83	8.5	1.5
Endrin	87	9.2	1.0
4,4′-DDD	79	8.6	0.5
2,4′-DDT	81	7.9	0.1
4,4′-DDT	88	8.3	0.05

Jiang et al., 2000; Samia et al., 2000; Zhulidov et al., 2000). Several monitoring projects have been conducted in Northern Vietnam since 1992 in order to determine the organic chlorinated pesticides in biota, soil, sediment, and in various foodstuffs (Iwata et al., 1994; Quyen et al., 1995; Nhan et al., 1998, 1999, 2001). In these works, DDTs were very often detected in all environmental compartments, it was also an indispensable consequence of the use of DDTs in a long time against malaria (Table 1). However, there was no systematic monitoring project involving the investigation of chlorinated pesticides in surface waters in Hanoi.

In this work, the determination of 15 selected pesticides (Table 2) in water samples collected from 30 sites in the area of Hanoi was undertaken. The analysis procedure for the qualification and quantification of organic chlorinated substances was initially selected, modified and then applied. A gas chromatography coupled with electron capture detector (GC–ECD) was used for the analysis (qualification and quantification). The different capillary columns were tested before with standard chlorinated pesticides to determine their separation. The qualification was reconfirmed using a gas chromatography coupled with mass spectroscopy (GC–MS).

2. Experimental

2.1. Materials and reagents

Chemicals, including chlorinated pesticides, and the solvents *n*-hexane and methanol were supplied by Riedel de Haeen Co. Ltd, Germany, at reagent grade quality (>99.8% purity). The octadecyl (1 g/6 ml Isolute) cartridge used as a sorbent for solid phase extraction was obtained from Baker (USA).

2.2. Sampling

The water samples were transferred to cleaned, air-free bottles with conical shoulders (5 l nominal volume for samples from rivers and irrigation canals and 10 l nominal volume for samples from lakes and wells).

2.3. Analytical methods

2.3.1. SPE clean-up

Solid phase extraction is a proven technique for traditional solvent extraction for the separation and enrichment of middle- or heavily volatile organochlorine pesticides from water. A solvent extraction of the water samples for the clean-up process was performed as described by Baker (1997). A column (cartridge) of octadecyl (1000 mg/6 ml Isolute) in a Baker spe-12 G system, was conditioned using a flow of 1 ml min^{-1} and applying 3 ml *n*-hexane, 3 ml methanol and flushed with 6 ml of distilled water, before the vacuum was released. 5 l (river and irrigation canal) or 10 l (lake and well) water samples were filtered using a fibre glass filter funnel and drawn through the conditioned octadecyl column, while the vacuum was controlled at 400 mbar. At the end of the adsorption process, the column was dried by purging with nitrogen and then rinsed with 5×1 ml *n*-hexane. The total extract was dried through sodium sulphate, concentrated to 1 ml under a stream of nitrogen and was analysed using GC–ECD.

The recovery rates and standard deviations of the clean-up method are given in Table 2. The volume of the water samples influenced the recovery rate. For this work, the recovery rate was determined for 5 and 10 l of water samples. The water samples were dosed with the pesticide pro analysis at a concentration of 100 ng l^{-1}. The specified values were calculated in each case via six measurements. The calculated recovery rates were stable and corresponded to the guidelines of the supplier Baker. This procedure was applied to the preparation of water samples between November 1998 and September 1999 in Hanoi.

2.3.2. GC–ECD and GC–MS

The qualitative and quantitative determination of chlorinated pesticides was performed using a gas chromatography Fisons Instruments GC 8000 series, electron capture detector ^{63}Ni-ECD (GC–ECD). The column for GC–ECD was a HP-5-MS capillary (30 m × 0.25 mm i.d., 0.25 μm film thickness). Helium 5.0 was used as carrier gas for the system (75 Psi, 1 ml min^{-1}). The make-up gas was argon/methane (ECD-Quality)

165 Psi. The temperature of the injector was 250 °C and the temperature of the detector was set to 300 °C. The oven temperature programme was: start ($t = 0$) at 60 °C, 7 °C min^{-1} to 160 °C and 4–280 °C. The injection volume was 3 μl in the splitless mode. The qualitative and quantitative detection of the organochlorine pesticides was accomplished by comparison of retention times and peak areas with a corresponding standard substance (Fig. 2). The application of one internal standard during gas chromatographic analysis is recommended to minimise systematic errors. The internal standard used in this work was 2,4,5-trichlorbiphenyl (TCB), which separated well from all gas chromatographic analysed organochlorine pesticides and has physicochemical properties similar to those of the analysed substances.

The qualitative determination was reconfirmed using GC–MS. The GC–MS is a Finnigan MAT, EI-ITS 40 (Electron Impact Ion Source, Ion Trap MS Detector). The capillary column was the same one, which used for GC–ECD. Helium 5.0 was used as carrier gas for the system (75 Psi, 1 ml min^{-1}). The chromatographic temperature programme for GC–MS was: start ($t = 0$) at 60 °C followed by a 10 °C min^{-1} increase to 160 °C and 4–250 °C maintaining this final temperature for 10 min. Temperature of the injector was set to 250 °C, transfer line: 270 °C. The injection volume was 4 μl in the splitless mode.

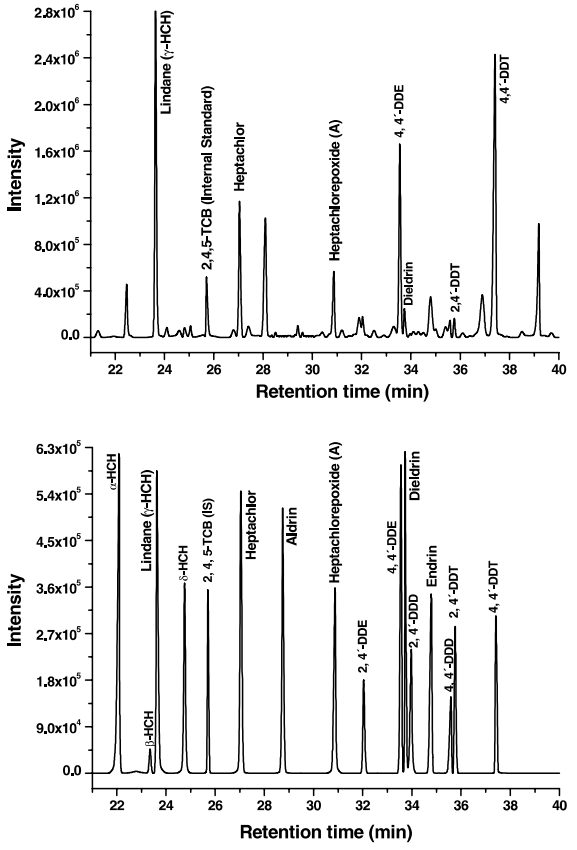

Fig. 2. Chromatograms of a real sample from sampling point P5 (upper) (November 1998, dry season) and of a blank water sample (lower) (15 organochlorine pesticides and an internal standard 2,4,5-TCB) obtained by GC–ECD.

3. Result and discussion

Numerous investigations of chlorinated pesticides in the environment of Hanoi have been carried out in different environmental compartments, including soil, sediment and fresh water biota (Tu, 1994; Hoa, 1995). In the report by Nhan et al. (1998), sediments and freshwater organisms of irrigation canals and rice fields were collected for investigation from two places in Hanoi in the rainy season (November 1995) and in the dry season (July 1996) and also from the Balat estuary of the Red river. Five other water samples collected from lakes and irrigation canals of plant-vegetable areas in Hanoi were also analysed by other research group (Doanh, 1998). Nhan et al. (1998) detected chlorinated pesticides in nearly all samples. However, they occurred only in some water samples taken from farming areas and at rather low concentration (from 1 to 6.5 ng l^{-1}). The present study had been undertaken in order to estimate more precisely and concretely the distribution of banned chlorinated pesticides in Hanoi waters, including rivers, irrigation canals, lakes and wells. For the first time, water samples (Fig. 3) taken from surface water in Hanoi were systematically analysed in this work in order to investigate their contamination.

The concentration values of organochlorine pesticides detected in water samples from areas of Hanoi in November 1998 and August 1999 are presented in Figs. 4 and 5. The analysis showed clearly the residues of lindane, heptachlor, aldrin, endrin, 4,4′-DDT at most of sampling points. The concentration of lindane in rivers ranged between 1.62 and 85.92 ng l^{-1}, endrin from 1.22 to 168.87 ng l^{-1} and especially 4,4′-DDT from 1.55 to 178.60 ng l^{-1} above those of the other pesticides. The results indicate that many pesticides still today exist as relevant pollutants.

The Red river (with a length of more than 1000 km) arises from Yunnan (South China), runs through North Vietnam and Hanoi before emptying into Tonkin Bay at the Balat estuary. The Red river is the second largest river in Vietnam after the Mekong river (south Vietnam) and the Duong river is a branch of the Red river. It is important to review other previous works related with the contamination of organochlorine pesticides in the environment in China, because the Red river can transport a certain amount of pesticides from pollution sources in China into the Red river delta of North Vietnam. Vietnam's neighbour China has a great influ-

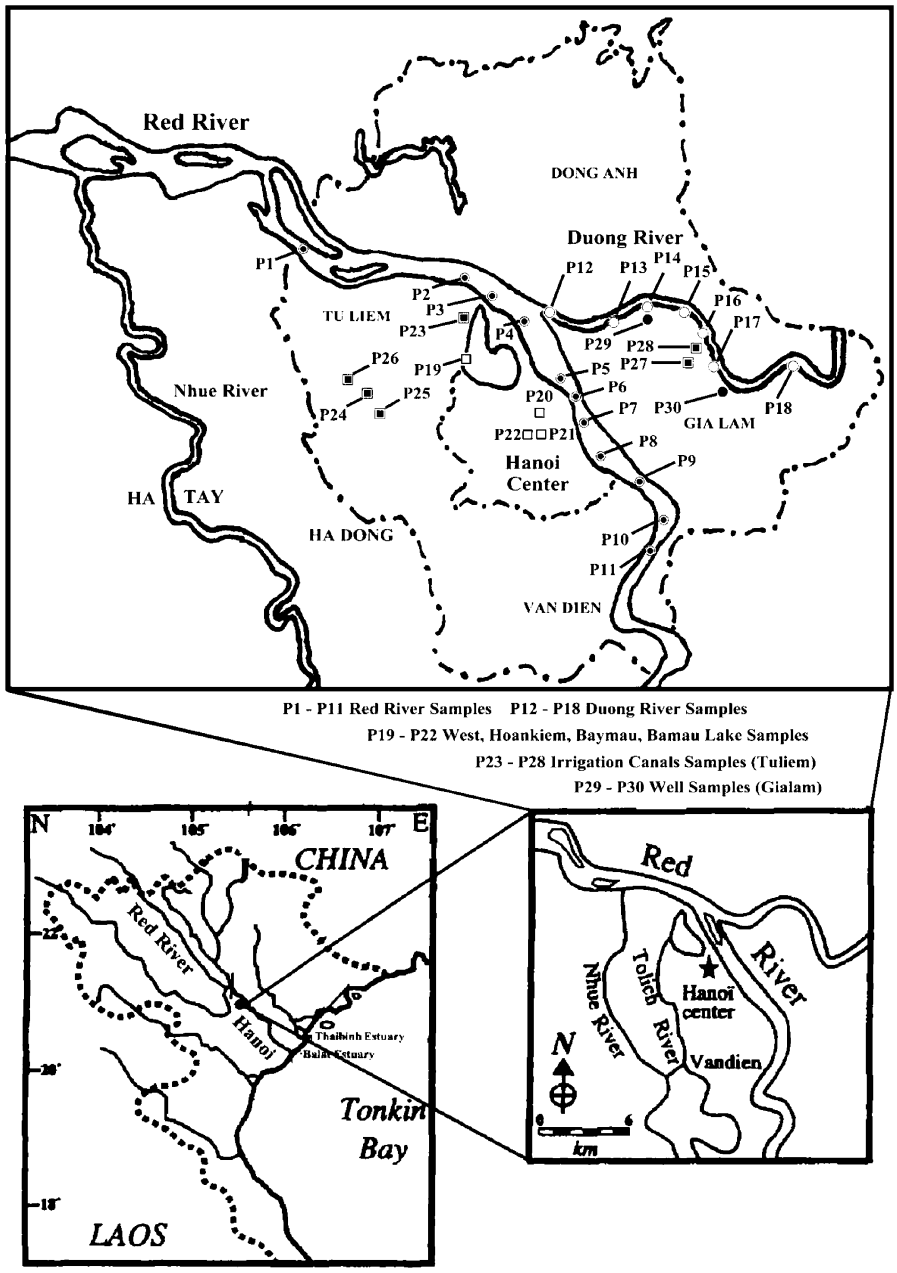

Fig. 3. The sampling map of Hanoi, North Vietnam (see also Nhan et al., 1998).

ence on Vietnamese markets. Every year, Vietnam imports a large amount of pesticides from abroad, partly from China. Technical HCH mixture (α: 67%, β: 10%, δ: 15%, γ: 8%) and DDT had been used in China as low cost broad band insecticides. In China, the annual production of the HCHs in 1980 was 240 000 tons, but its usage was banned already in 1983 (Hua and Shan, 1996). Water and sediment samples of the Yangtse river, the third largest river in the world and the largest river in China, were studied in that work. The mean concentrations of all HCH isomers in water samples from the Yangtse river were relatively stable, ranged between 9.27 and 10.50 $ng l^{-1}$ and much higher than the values of other pesticides, including DDT (Jiang et al., 2000). In comparison with the rather high lindane (γ-HCH) concentration (from 1.62 to 85.92 $ng l^{-1}$) and the low

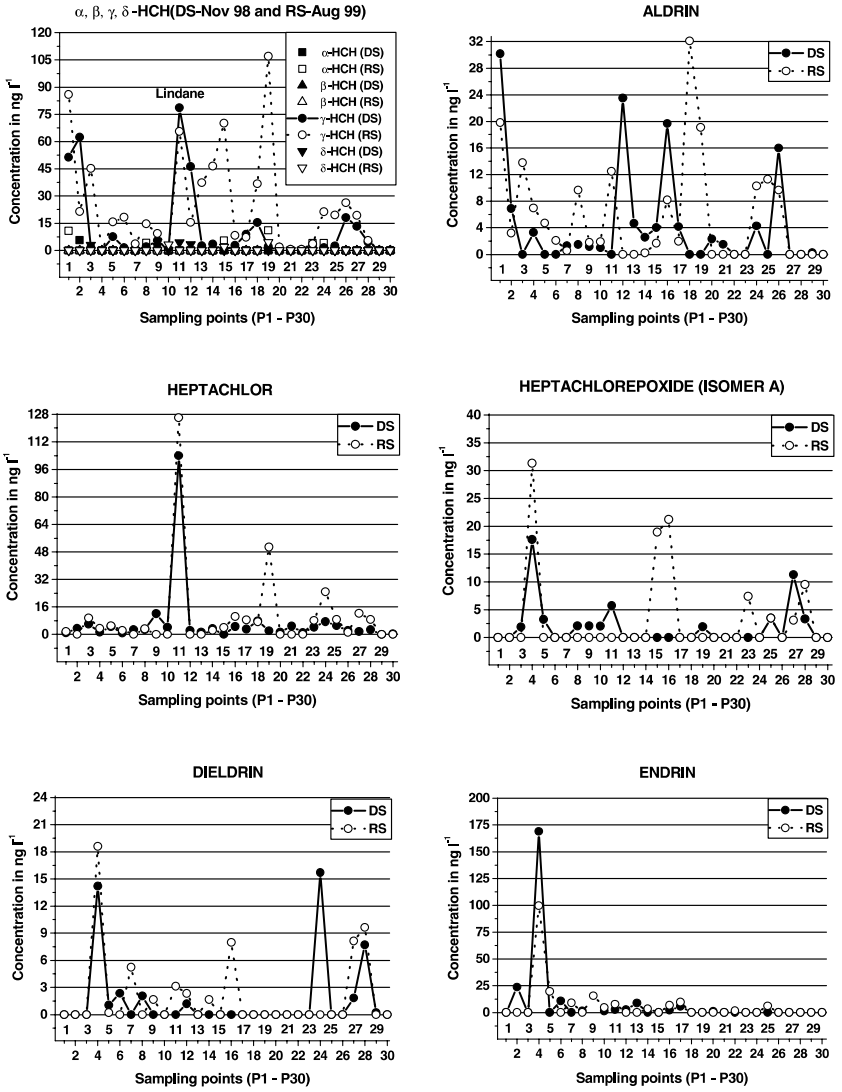

Fig. 4. Levels of HCHs and other chlorinated pesticides at different sampling points (P1–P30) in Hanoi (DS: dry season, RS: rainy season).

concentrations of α,β,δ-HCH in the Red river, it is apparent that the Red and the Duong rivers are mostly contaminated only by lindane, while the Yangtse river is contaminated only by the other HCH-isomers. It probably means that pure lindane was used in Vietnamese agriculture more than the technical HCH mixture as used mostly in China and the pollution sources are in the local regions (Red river delta, North Vietnam), but not from China.

Moreover, other investigations had showed that lindane was detected with low concentration in soil and sediment (Nhan et al., 1998, 2001). This means a large amount of lindane can be released from soil to waters during the rainy season. Nhan et al. (1998) had found that the amounts of lindane in sediments (from irrigation canals, rice fields in Hanoi, Vietnam and from the Delta of the Red river) were consecutively lower in the rainy season (July 1996, dry weight from 0.025 to 0.16 $ng\,g^{-1}$) than in the dry season (November 1995, 0.14–0.62 $ng\,g^{-1}$) by an average factor of 7. In comparison to the results of our work, it is noted that the concentrations of lindane in the Red and Duong rivers in the rainy season (August 1999, of 3.56–85.92 $ng\,l^{-1}$) were also slightly higher than in the dry season (November 1998, of 1.55–78.61 $ng\,l^{-1}$) (Fig. 4). The mean concentration of ΣHCHs in the rivers in the RS (29.3 ± 117 $ng\,l^{-1}$) was definitely higher than in the DS (17.2 ± 71.8 $ng\,l^{-1}$) (Table 3). HCHs were detected with relative high

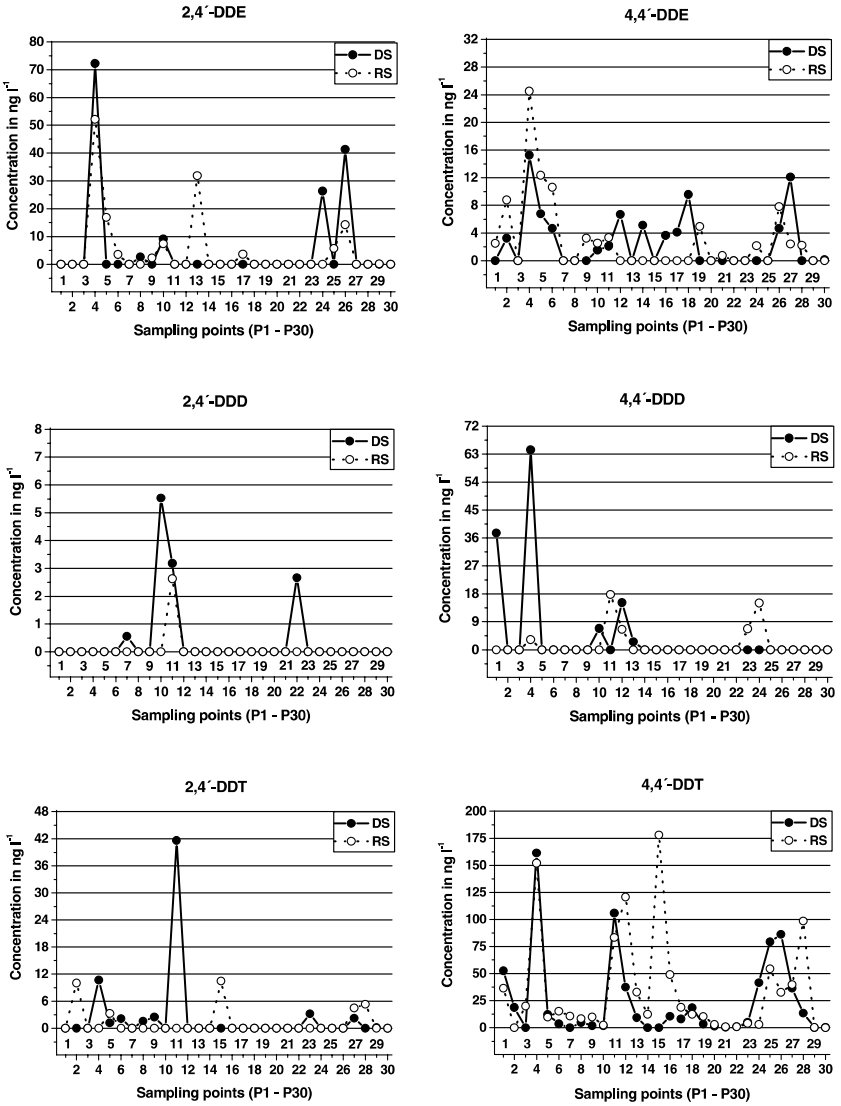

Fig. 5. Levels of DDTs at different sampling points (P1–P30) in Hanoi (DS: dry season, RS: rainy season).

concentration in the lakes in the RS (31.7 ± 60.4 ng l^{-1}), especially in West lake (Ho Tay) with concentration of HCHs in the RS was 122 ng l^{-1}. Ho Tay is a part of Red river long time ago and it still has some small canals adjoined with the Red river. The water quality of Ho Tay can be affected partly from the Red river, that can also explain why in the other three lakes in the centre of Hanoi, HCHs were detected with very low concentration, just from 0.26 ng l^{-1} in the DS to 3.13 ng l^{-1} in the RS. Concerning with the considerable concentrations of HCHs in irrigation canals, the reason is the water samples were collected at six canals, which adjoined with Nhue river (is connected to Red river at times annually for irrigation) and Duong river. HCHs were determined here with mean concentrations between 7.19 ± 6.82 (DS) and 17.3 ± 8.79 ng l^{-1} (RS). HCHs were also detected in two water samples of wells near the Duong river with low mean concentrations from 0.04 ± 0.05 ng l^{-1} (RS) to 0.21 ± 0.02 ng l^{-1} (DS). Not many well samples were collected because most of the people in this area (centre and near centre of Hanoi) are using treated underground water (from the depth of more than 30 m supplied by waterworks) as drinking water.

The highest concentration of HCHs detected at sampling station 1 (Red river) in the rainy season (96.7 ng l^{-1}) is nevertheless much lower than their allowable limit in surface waters (<15 μg l^{-1}) according to Criteria of Vietnam (1995). However, Doanh (1998) had detected

Table 3
Mean concentrations of chlorinated pesticides ($ng\,l^{-1}$) in surface waters of the Red river (P1–P11), Duong river (P12–P18), lakes (P19–P22), irrigation canals (P23–P28) and wells (P29–P30) in November 98 and August 1999

	ΣHCHs		Heptachlor		Aldrin		Heptachlor Epoxide(A)		Dieldrin		Endrin		ΣDDTs	
	DS	RS	DS	RS	DS	RS	DS	RS	DS	RS	DS	RS	DS	RS
Red river														
P1	51.3	96.7	0.91	1.63	30.2	19.8	<0.5	<0.5	<0.1	<0.1	<1.0	<1.0	90.2	38.8
P2	68.1	21.4	3.58	<0.025	6.89	3.19	<0.5	<0.5	<0.1	<0.1	23.6	<1.0	21.9	18.8
P3	4.48	45.2	6.06	9.56	<0.5	13.8	1.92	<0.5	<0.1	<0.1	<1.0	<1.0	<DL	20.0
P4	<DL	<DL	1.28	3.54	3.31	6.98	17.6	31.3	14.2	18.6	169	99.6	324	232
P5	7.52	15.7	4.49	5.10	<0.5	4.73	3.25	<0.5	1.03	0.21	<1.0	19.6	20.0	42.0
P6	1.55	18.3	0.81	2.26	<0.5	2.12	<0.5	<0.5	2.35	<0.1	10.8	<1.0	10.2	29.3
P7	<DL	3.56	2.83	<0.025	1.30	0.56	<0.5	<0.5	<0.1	5.23	<1.0	8.97	0.55	10.7
P8	2.06	18.8	2.84	3.21	1.49	9.70	2.11	<0.5	2.08	<0.1	1.48	<1.0	8.71	8.4
P9	8.67	9.26	12.1	<0.025	1.17	1.81	2.13	<0.5	<0.1	1.68	<1.0	15.6	4.06	15.2
P10	<DL	3.12	4.09	<0.025	0.98	1.89	2.07	<0.5	<0.1	<0.1	1.22	4.65	24.6	12.2
P11	83.0	65.6	104	126	<0.5	12.5	5.72	<0.5	<0.1	3.15	2.68	7.82	153	107
Duong river														
P12	49.6	15.5	2.31	<0.025	23.5	<0.5	<0.5	<0.5	1.20	2.33	2.65	<1.0	59.2	127
P13	2.61	37.3	1.32	<0.025	4.65	<0.5	<0.5	<0.5	<0.1	<0.1	8.84	<1.0	11.7	64.5
P14	3.54	46.5	3.32	2.37	2.57	0.23	<0.5	<0.5	<0.1	1.68	<1.0	3.50	5.15	12.4
P15	<DL	77.5	<0.025	4.02	4.04	1.67	<0.5	18.9	<0.1	<0.1	<1.0	<1.0	<DL	189
P16	2.82	8.23	4.65	10.4	19.7	8.20	<0.5	21.2	<0.1	7.98	2.11	6.54	14.2	48.9
P17	8.79	7.25	3.16	8.51	4.18	1.96	<0.5	<0.5	<0.1	<0.1	5.55	9.62	12.3	22.3
P18	15.4	36.7	7.82	7.46	<0.5	32.1	<0.5	<0.5	<0.1	<0.1	<1.0	<1.0	27.9	12.4
Mean ± S.D.	17.2 ± 71.8	29.3 ± 117	17.4 ± 23.8	19.3 ± 29.0	11.0 ± 29.0	12.8 ± 8.44	3.66 ± 4.22	7.52 ± 9.40	2.19 ± 3.33	4.30 ± 4.64	25.3 ± 40.5	18.5 ± 23.2	43.7 ± 79.9	56.1 ± 65.6
Lakes														
P19	2.16	122	2.15	50.8	<0.5	19.1	1.96	<0.5	<0.1	<0.1	<1.0	<1.0	3.35	15.3
P20	<DL	3.13	1.36	<0.025	2.33	<0.5	<0.5	<0.5	<0.1	<0.1	0.89	<1.0	1.32	2.76
P21	0.26	0.74	4.84	<0.025	1.51	<0.5	<0.5	<0.5	<0.1	<0.1	<1.0	<1.0	0.21	1.55
P22	0.35	0.69	1.12	<0.025	<0.5	<0.5	<0.5	<0.5	<0.1	<0.1	<1.0	1.61	3.58	0.65
Mean ± S.D.	0.69 ± 0.99	31.7 ± 60.4	2.37 ± 1.71	12.7 ± 25.4	0.96 ± 1.16	4.77 ± 9.55	0.49 ± 0.98	<0.5	<0.1	<0.1	0.22 ± 0.45	0.40 ± 0.81	2.12 ± 1.63	5.07± 6.88

Irrigation canals													
P23	3.15	7.78	4.16	8.20	<0.5	<0.5	<0.5	7.40	<0.1	<0.1	<1.0	<1.0	8.16	10.7
P24	1.58	25.4	7.49	24.8	4.29	10.3	<0.5	<0.5	15.7	<0.1	<1.0	<1.0	67.8	20.2
P25	2.45	19.5	5.11	8.71	<0.5	11.3	3.47	3.47	<0.1	<0.1	<1.0	6.12	79.4	59.9
P26	18.1	26.3	2.32	1.23	16.0	9.69	<0.5	<0.5	<0.1	<0.1	<1.0	<1.0	132	54.7
P27	13.2	19.3	1.72	12.2	<0.5	<0.5	11.3	3.11	1.84	8.14	<1.0	<1.0	50.7	46.5
P28	4.63	5.46	2.69	8.69	<0.5	<0.5	3.35	9.53	7.72	9.65	<1.0	<1.0	13.3	106
Mean ±	7.19 ±	17.3 ±	3.92 ±	10.6 ±	3.38 ±	5.21 ±	3.02 ±	3.92 ±	4.21 ±	2.97 ±	<1.0	1.02 ±	58.6 ±	49.7 ±
S.D.	6.82	8.79	2.15	7.79	6.40	5.73	4.39	3.88	6.36	4.62		2.50	46.0	33.8
Wells														
P29	0.22	<DL	<0.025	0.05	0.25	<0.5	<0.5	<0.5	0.21	<0.1	<1.0	<1.0	0.11	0.17
P30	0.19	0.07	0.33	<0.025	<0.5	<0.5	<0.5	<0.5	<0.1	<0.1	<1.0	<1.0	0.23	<DL
Mean ±	0.21 ±	0.04 ±	0.17 ±	0.03 ±	0.13 ±	<0.5	<0.5	<0.5	0.11 ±	<0.1	<1.0	<1.0	0.17 ±	0.09 ±
S.D.	0.02	0.05	0.23	0.04	0.18				0.15				0.08	0.12

DS: dry season (November 1998); RS: rainy season (August 1999); DL: detection limit; S.D.: standard deviation.

lindane in two sampling points (canals) near West lake (Hanoi) and found its much higher concentration varied between 8 and 10 $\mu g\,l^{-1}$. Most of the work related with the monitoring of organochlorine pesticides in Vietnam were focused on soil, sediment, food and biota samples, but not in waters. Just in a recent work, the contamination of these compounds in water has been investigated at Tamgiang-Cauhai Lagoon in Hue (central part of Vietnam) (Khoa et al., 2000). In that work, there were no HCHs, aldrin, heptachlor, endrin, dieldrin detected.

Chlorinated cyclodienes, including aldrin, dieldrin and endrin could not be detected in the waters of the Red river in 1996 and 1997 (in only two collected samples) between Hanoi and the sea coast, because cyclodiene had never been used in Northern Vietnam in meaningful amounts (Nhan et al., 1998). In contrast, in 1998 and 1999, chlorinated cyclodiene was found now by us in nearly all water samples taken from the Red and Duong rivers (Fig. 4, Table 3). Aldrin and endrin appeared more often with their mean concentrations decreased following the order: river > irrigation canal > lake > well. The concentration of aldrin was highest in rivers in the rainy season: $12.8 \pm 8.44\ ng\,l^{-1}$ and the concentration of endrin was highest in rivers in the dry season: $25.3 \pm 40.5\ ng\,l^{-1}$. Aldrin and endrin were not detected in some sampling points (irrigation canals and lakes), while dieldrin only appeared in some water samples (rivers and irrigation canals) with mean concentrations of 2.19 ± 3.33 (DS), $4.30 \pm 4.64\ ng\,l^{-1}$ (RS) and 4.21 ± 6.36 (DS), $2.97 \pm 4.62\ ng\,l^{-1}$ (RS), respectively. The results show that these compounds probably originate from supraregional, atmospheric or river flow transport into the surface waters of Vietnam.

DDT had been imported and used since 1957 and up to 1994 (Table 1), it was stopped in Vietnam due to its high toxic and long time residue in environment. At present, only chemicals belong to Pyrethroid group are in use for malaria control in Vietnam (Hien, 1999). DDTs were used by applying residual spraying method in highlands, remote areas and border line with large amount from 1957 to 1979. From 1985, the used amount of DDTs was decreased. However, due to lack of knowledge and management of using DDTs, they are still recently used for crop protection and controlling of mosquito and other insects. DDT may be metabolised easily to DDE and DDD in the environment, its derivatives are more stable and more persistent than DDT itself (Bossi et al., 1992; Heinisch, 1992). 4,4′-DDT was also used in China for a long time as an insecticide. In most analysed sediments of the Yangtse river (China), 4,4′-DDE occurred in relatively high concentrations (4.3 $ng\,g^{-1}$ dry weight). In one sample, 4,4′-DDT reached its top concentration (2.7 $ng\,g^{-1}$ dry weight). In water samples of this river, 4,4′-DDT and its derivatives were

found in very low concentrations (< 2 ng l^{-1}) (Jiang et al., 2000).

Nhan et al. (1998) have shown that DDT occurs in sediments of rice fields in Red river delta in higher concentrations (7.0–7.5 ng g^{-1} dry weight) compared with those in sediment at the sea coast (5.8–7.3 ng g^{-1} dry weight). In the rainy season, the concentration of DDT in the sediments of the Red river increased considerably. The derivatives of 4,4′-DDT were also determined as expected, e.g. 4,4′-DDD (from 2.54 to 64.3 ng l^{-1}), 2,4′-DDE (2.22–72.2 ng l^{-1}) as well as 4,4′-DDE (1.54–24.5 ng l^{-1}). However, 4,4′-DDE had a higher concentration in sediments (1.52–10.2 ng g^{-1}) than 4,4′-DDT (0.51–2.43 ng g^{-1}). In freshwater and marine molluscs, the concentration of DDTs was relatively high, in the range of 78–90 and 17–24 ng g^{-1}, respectively. This concentration difference in chlorinated compounds primarily reflects the higher concentrations of DDTs in the Red river valley in comparison with the coastal sea, as observed in the sediments of this area (Nhan et al., 1998). Their observations also correspond with the results of this work, that DDTs were found at considerable concentrations in water samples of the Red and Duong rivers (Fig. 5).

4,4′-DDT was found in concentrations of between 2.31 and 178.60 ng l^{-1} in most of 18 water samples analysed from the Red and Duong rivers. Its derivatives, like e.g. 2,4′-DDD, 4,4′-DDD, 2,4′-DDE, 4,4′-DDE, did not appear frequently either in the rainy or dry seasons. Although 4,4′-DDE is more persistent than 4,4′-DDT, the contamination of 4,4′-DDT in surface waters in the environment of Hanoi was relatively higher than that of 4,4′-DDE. Our results demonstrate that the residue concentrations of these illegal pesticides in water samples from rivers as well as from irrigation canals was higher than those from lakes and wells (Fig. 5, Table 3). Table 3 shows the mean concentrations of ΣDDTs in the rivers were not quite different with that in irrigation canals: 43.7 ± 79.9, 58.6 ± 46.0 ng l^{-1} in the dry season and 56.1 ± 65.6, 49.7 ± 33.8 ng l^{-1} in the rainy season, respectively. DDTs were also detected in lakes with low concentration: 2.12 ± 1.63 in the dry season and 5.07 ± 6.88 ng l^{-1} in the rainy season. Their concentrations in two well water samples were very low, ranged between 0.11 and 0.23 ng l^{-1}.

In comparison with the results reported in the recent work (Doanh, 1998): 4,4′-DDE: 5–9 μg l^{-1}, 4,4′-DDT: 4–7 μg l^{-1} in irrigation canals in areas of Hanoi, the concentrations of DDTs found in that study were especially higher than that in our investigation, with concentrations of 4,4′-DDE ranging from 2.17 to 12.15 ng l^{-1}, 4,4′-DDT from 3.01 to 98.62 ng l^{-1}. Concerning with the work of Khoa et al., 2000 at Tamgiang-Cauhai Lagoon (Hue), the concentrations of ΣDDTs in waters there were very low and ranged between 7 and 90 pg l^{-1}.

4. Conclusion

In four HCH isomers investigated, only lindane was appeared in most of sampling points with considerable concentrations. The results show the consequence of using a large amount of lindane (or "666" insecticide), which is very popular in Vietnam up to 1993. The contamination of lindane in the surface waters of Hanoi is caused by its release from the contaminated soil or sediment in the area of Red river delta, granary of North Vietnam, during the rainy season, corresponding with its low concentration in soil and sediment in the previous and recent works (Nhan et al., 1998, 1999, 2001). Moreover, in comparison with recent work investigated in Hue (central part of Vietnam) (Khoa et al., 2000), there was no lindane detected, that was logical because Hue is not a granary and the amount of pesticides used is not significant.

Chlorinated cyclodienes, including aldrin and endrin; heptachlor and heptachlorepoxid (isomer A) were detected at most of the sampling points with remarkable concentrations, dieldrin was detected in only some samples. There is no information related with their significant amount used in the past in Vietnam, therefore they can be transported through Red river flow or atmosphere from other regions near the border with China.

DDTs were detected with highest concentrations in 15 analysed insecticides consecutively for two years from November 1998 to August 1999. It showed the deep impact of using DDTs in malaria control in North Vietnam into the environment. The contamination of DDTs spreads over the large areas of Red river delta, if other recent works related with the contamination of DDTs in soil, sediment and in biota are reviewed.

Although the application of the pesticides investigated in this report has been illegal in Vietnam for several years, they still contaminate the waters of Hanoi at considerable concentrations, especially in the rivers and in the irrigation canals. This study will contributes with other previous investigations for assessment of influence of organochlorine pesticides on different environmental compartments (water, soil, sediment, biota, etc.) of Red river delta.

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