

EVALUATION OF ORGANOCHLORINATED PESTICIDE RESIDUE IN THE WATER OF BA TRI AGRICULTURAL CANAL BEN TRE PROVINCE

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ABSTRACT

The residues of Organochlorine pesticides from the water of the agricultural canal and river in Ba Tri district, BenTre province were determined by gas chromatography with electron-capture detector. The solid phase extraction (SPE- C₁₈) cartridge was applied to extract organochlorine pesticides residues in water samples. The samples were collected during the dry, wet season and the crop growing 2006-2007. The results showed that most of water samples were contaminated with pesticide at concentration from 0.01 to 2.00 ppb. The residue of pesticides in water mainly depended on the crops season and have highest value in the beginning of growing period. The concentration of pesticides residues decreased from rice- field to canal and river. There were many forbidden pesticide such as HCH, Endosulfan, Heptachlor, Dieldrin etc. have been found with high frequency in water. It causes a big risk for human health and aquatic biota.

I - INTRODUCTION

Ba Tri district of Ben Tre province, Vietnam mainly rice growers, gain 50% rice yield of Ben Tre province, each year. With expectations in reducing crop losses, the farmers started using more and more pesticides. Organochlorine pesticides have been used extensively in agriculture and are very persistent in nature. Using too much pesticide in agriculture causes soil, water and food to become contaminated with pesticides. Therefore, as pesticides have become essential components of modern agricultural systems and they also have become public health issues.

Very few studies that determine the levels of the organochlorine pesticide residues in water and their impact to aquatic biota conducted in Vietnam

The objective of the current study was identification and quantification of organochlorine pesticides residues in water from rice field, canal, and river of Ba Tri district of Ben Tre province during growing time. To assess the potential risks of such residual pesticides and what levels they affect to aquatic organisms in comparison with establish acceptable limits of Vietnam.

II - MATERIALS AND METHOD

Description of the study area

The Ba Tri district of Ben Tre province, Viet Nam is situated at the end of Bao Island, between Ba Lai and Ham Luong River. The Ba Tri district is bordered by Binh Dai, Giong Trom and Thanh Phu district, with agricultural land around 37000 ha, average yielding around 164000 tons rice per year [7].

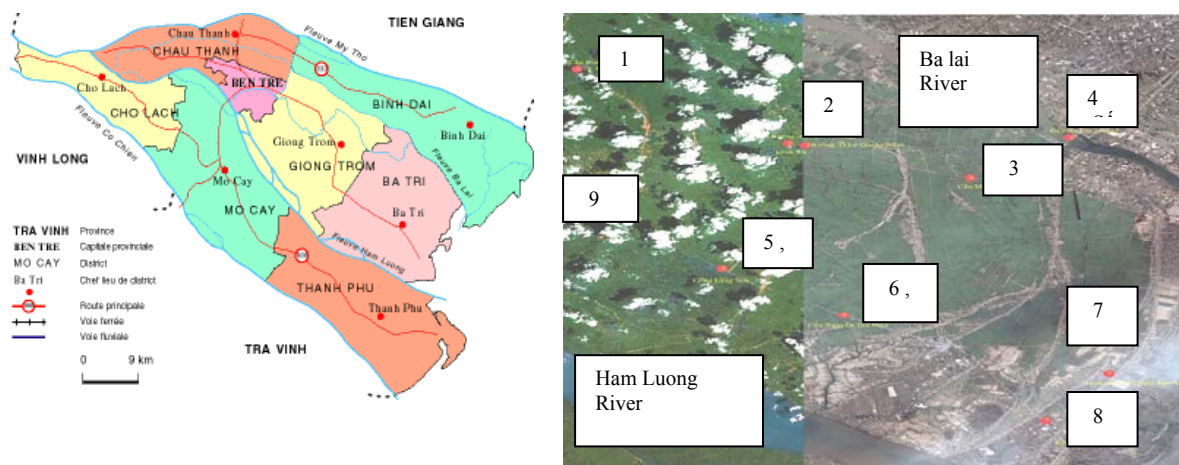


Figure 1: Map of Ben Tre province

Sampling station: No. 1: Binh Chanh canal, No. 2: Canal 9A, No. 3: My Quy canal No. 4: Ba Lai dam; No. 5: Cai Bụng canal, No. 6: An Binh Tay canal, No. 7: Tan Thuy canal, No. 8: Rach Ra canal, No. 9: Hung Nhuong, Giong Trom

Sampling

Samples were collected from the canal to the river. Sampling stations are described in figure 1.

Samples were collected following three growing times (winter - spring: from November to February; summer - autumn: from March to June; autumn - winter: from July to November).

From December to April is dry season; from May to November is rainy season

Samples were collected and preserved following Vietnamese Standard: TCVN 5992-1995, TCVN 5996-1995, TCVN 6000-1995, TCVN 5993-1995. Some parameters such as pH, DO were measured at the field.

Gas Chromatographic Analysis

Solid Phase Extraction (SPE) was used for the extraction of organochlorine pesticides residues in water sample [1 - 6]. The collected water sample was pre-treatment by supersonic and pre-filtered to remove particulate matter and were acidified to pH = 2. Prior to the extraction, the cartridge C-18 bonded phase were wash with mixture solvent (Dichloromethane: Acetone: water = 1: 1: 1), the acidification water sample was passed through the cartridge with flow rate 10 - 15 ml/min under vacuum. After sample extraction, suction

continued for 15 min to dry packing material inside cartridge. The pesticides trapped in the C-18 bonded phases was eluted by passing Dichloromethane and fraction was evaporated in a gentle stream of Nitrogen and the organochlorine pesticides were eluted with n-hexane before inject to Gas Chromatography (GC).

The samples were then analyzed with Shimadzu T2010 GC fitted with ECD detector and Equipt-5 column (30 m × 0.32 mm i.d.×0.25 μm), following standard method of EPA 608, EPA 614, EPA 619, EPA 630 and EPA 632. Identification and quantification were accomplished using external reference standards and relative retention time techniques. The GC parameters and operational conditions were shown in table 1.

III - RESULTS AND DISCUSSION

1. Organochlorine pesticides residues detected in surfaces water from Ba Tri district of Ben Tre province, Vietnam

The concentration of organochlorine pesticides residues in surfaces water from Ba Tri district of Ben Tre province was shown in table 2.

Table 1: The GC parameters and operational conditions detected pesticides

Parameters	Conditions
Temperature of sample gasification	230°C
Temperature of ECD detector	290°C
Temperature of column (temperature program 4 ^o /min)	80-290°C
Flow of nitrogen carrier	2 ml/min
Ratio of split less	1:10
Volume of sample injection	1µl

- Evaluation of pesticide in water following certain criteria and guidelines: TCVN 5941-1995, TCVN 530-1995, EPA MCLs-1991. One-way analysis of varian (ANOVA) was used to determine the statistical significant different ($p < 0.05$)

Table 2: Organochlorine pesticides residues detected in surfaces water from Ba Tri district, Ben Tre province, Vietnam (Investigation year 2006-2007)

Sampling station	Sampling location	Pesticides residues concentration detected (ppb)							
		Year 2006			Year 2007				
		May	July	Nov.	Feb.	May	July	Sept.	Nov.
No. 1	1	0.049	0.265	0.258	0.064	0.260	0.256	0.331	0.238
No. 2	2a	0.450	0.588	0.330	0.350	0.388	0.326	0.394	0.249
	2b	0.350	0.258	0.640	0.110	0.436	0.365	0.376	0.411
	2c	0.520	1.033	0.200	0.330	0.474	0.428	0.360	0.420
No. 3	3a	0.630	2.104	0.710	0.440	0.285	0.624	0.520	0.550
	3b	0.390	0.801	0.200	0.320	0.465	0.367	0.505	0.380
	3c	0.260	0.380	0.570	0.100	0.952	0.293	0.456	0.350
No. 4	4	0.310	0.462	0.320	0.033	0.239	0.390	0.329	0.289
No. 5	5	0.644	0.662	0.650	0.364	0.267	0.407	0.418	0.135
No. 6	6a	0.241	0.263	0.427	0.064	0.285	0.376	0.477	0.260
	6b	0.747	0.390	0.292	0.180	0.266	0.239	0.498	0.230
No. 7	7a	0.145	0.227	0.240	0.093	0.198	0.306	0.377	0.183
	7b	0.151	0.289	0.240	0.150	0.240	0.414	0.607	0.520
No. 8	8	0.260	0.460	0.410	0.120	0.366	0.407	0.520	0.230
No. 9	9	0.410	0.380	0.300	0.280	0.293	0.511	0.480	0.410

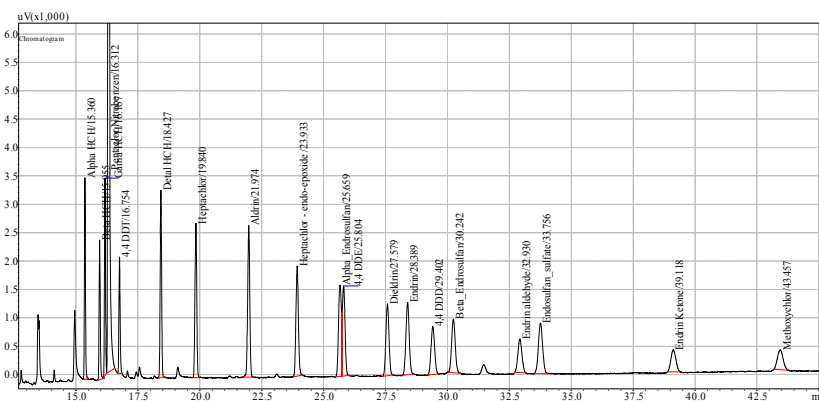


Figure 3: Gas Chromatogram of 18 organochlorine pesticides

All the samples analyzed were found to be contaminated with organochlorine pesticides at concentration range from 0.049 to 2.104 ppb. Residues concentrations of organochlorine pesticides were higher than permissible limit (<0.5ppb) in 30% of the water samples [8]. At the Ba Lai dam, the concentrations of organochlorine pesticides residues in water were always lower than permissible limit it might be due to dilution by the water in the river. Although organochlorine pesticides residues

concentrations in the river were lower than establish acceptable limits of Viet Nam, however it might result in chronic effects to aquatic biota.

2. Evaluation of organochlorine pesticides residues in water during crops season 2006-2007

The concentration of organochlorine pesticides residues in water were shown in table 3.

Table 3: Concentration of pesticides residues detected in water during crops season

Growing Time		Concentration of pesticide residues (ppb)		
		Water in Field	Water in Canal	Water in Ba Lai dam
Winter - spring	Early crop	0.476	0.395	0.323
	Later crop	0.276	0.166	0.033
Summer - autumn	Early crop	0.436	0.354	0.310
	Later crop	0.375	0.343	0.320
Autumn - winter	Early crop	0.810	0.488	0.462
	Later crop	0.378	0.286	0.290

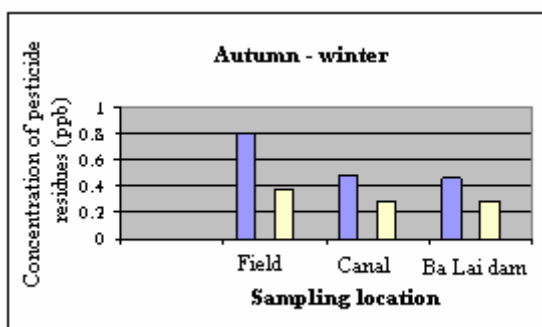


Figure 4: Variation of pesticides residues concentration detected during crops season

There was a marked difference in frequency of organochlorine pesticides residues in study area between early and late crops seasons. High frequencies of pesticides residues detection were observed at the beginning of crops season but the frequencies were lower at the harvesting time. Due to dilution, the pesticide concentration decreased from rice field to canal to river. However, until Ba Lai dam concentration of pesticides residues decreased only about \approx 30-50%, this indicated pesticides residues were very persistent in nature and can not degrade by microorganism.

3. Variation of concentration of organochlorine pesticides residues detected in dry and wet season

The concentration of organochlorine pesticides residues in water in dry and wet season were shown in table 4.

There was insignificantly difference of organochlorine pesticides residues in wet season samples compared to in dry season samples. Organochlorine pesticides residues were observed around 0.1 to 0.5 ppb in both wet and dry seasons. This indicated that the pesticides residues in the water samples of the field and the canal mainly depended on crop growing seasons.

4. Identification of forbidden pesticides detected in surface water from Ba Tri province, Vietnam

The result shows that there were around 10 to 15 species of forbidden pesticides detected in surface water from Ba Tri district of Ben Tre province, Vietnam. And these forbidden pesticides were stable and had a very long half-life time. Among these forbidden pesticides

such as Heptachlor, HCH and Endosulfan presented frequency, next were the DDT, Aldrin.

Following the investigation data (2006-

2007) [7], around 50% of pesticides used in agro-cultivation without source of supply. That indicated the farmers did not care about regulation and worked by sheer force of habit.

Table 4: Concentration of pesticide residues detected in dry and wet season

Sampling station	Sampling location	Concentration of pesticide residues detected (ppb)	
		Dry season	Wet season
No. 1	1	0.12	0.27
No. 2	2a	0.40	0.38
	2b	0.30	0.41
	2c	0.44	0.49
No. 3	3a	0.45	0.90
	3b	0.39	0.45
	3c	0.44	0.41
No. 4	4	0.12	0.36
No. 5	5	0.43	0.38
No. 6	6a	0.20	0.36
	6b	0.40	0.33
No. 7	7a	0.15	0.27
	7b	0.18	0.53
No. 8	8	0.25	0.41
No. 9	9	0.33	0.42

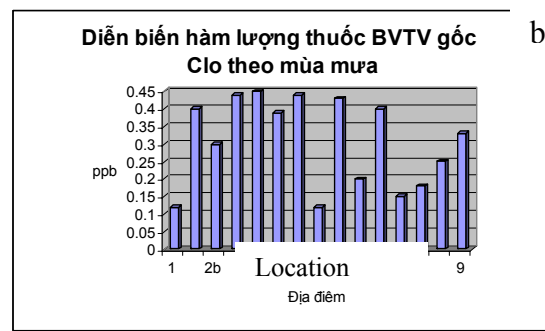
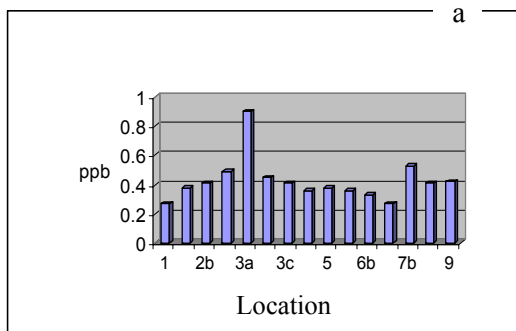


Figure 5: Variation of concentration of pesticides residues detected in dry (a) and wet season (b)

The very toxic pesticides such as BHC, Heptachlor, Lindan and DDT presented with quite high concentration and frequency. Comparisons of the results from our study to the water quality criteria and guidelines (TCVN 6774:20), the pesticides residues in the surface water from our study were higher than establish acceptable limits. It would be adverse effect to aquatic biota.

IV - CONCLUSIONS

- All the water samples from Ba Tri district of Ben Tre province, Viet Nam were contaminated with organochlorine pesticides at concentration range from 0.01 to 2.0 ppb.
- There was a marked difference in frequency of organochlorine pesticides residues in the study area between early and late crops

Table 5: List of forbidden pesticides detected in surface water from Ba Tri district, Ben Tre province, Vietnam (ppb)

No.	Forbidden Pesticides detected	High concentration	Low concentration	Medium concentration
1	Belta HCH	0.119	0.001	0.01
2	Alfa HCH	0.099	0.001	0.03 — 0.04
3	Gama HCH	0.101	0.001	0.04
4	4,4 DDT	0.087	0.001	0.07
5	Delta HCH	0.102	0.001	0.01 — 0.02
6	Heptachlor	0.146	0.001	0.03
7	Aldrin	0.060	0.001	0.01
8	Heptachlor — endo — epoxide	0.036	0.001	0.001
9	Alpha — endosulfan	0.070	0.001	0.001
10	4,4 DDE	0.020	0.001	0.001
11	Dieldrin	0.086	0.001	0.001
12	Edrin	0.069	0.001	0.001
13	4,4 DDD	0.020	0.001	0.001
14	Beta — edrosulfan	0.005	0.001	0.001
15	Edrin Aldehyde	0.460	0.001	0.05 — 0.06
16	Endosulfan — Sulfate	0.719	0.001	0.02 — 0.03
17	Edrin keton	0.073	0.001	0.04 — 0.05
18	Methoxychlor	0.542	0.001	0,001.

seasons. There was insignificantly difference of organochlorine pesticides residues in water samples between wet and dry seasons.

- There were 10 to 15 species of forbidden pesticides detected in surface water from Ba Tri district of Ben Tre province. The very toxic pesticides such as BHC, Heptachlor, Lindan and Eldrin presented with quite high concentration and frequency. It would be adverse effect to aquatic biota.

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REFERENCES

1. The Japan Society for Analytical Chemistry. Analytical Science, V21 (2005) 268.
2. Pesticides and water pollutants, www.fao.org.
3. Mohammad A Mottaleb and M. Z. Abedin. Determination of pesticides in soil by solid phase extraction — Gas Chromatography. Analytical Science March V. 15, 203 - 288 (1999).
4. J. Barmabas, J. Dean, M. Hitchen, P. Owen. Anal. Chim Acta., V. 291, 261 (1994).
5. G. Font, J. Manes, J. C. Motto, Y. Pico. J. Chromatogr. 135, 642 (1993).
6. C. Sanchez Brunete et al. J. Agric. Food. Chem., 52, 1445 (2004).
7. Nguyễn Thị Dung, Báo cáo tổng kết đề tài: Đánh giá dư lượng thuốc bảo vệ thực vật trong kênh rạch canh tác nông nghiệp tỉnh Bến Tre. Tp HCM- 2007.
8. TCVN 6774-20.

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Đánh giá dư lượng thuốc trừ sâu gốc Clo hữu cơ trong nước kênh rạch nông nghiệp huyện Batri tỉnh Bến tre .