นิพนธ์ต้นฉบับ

Detection of chlorinated hydrocarbon residues in catfish, shrimp, river water and sedimentation from natural source in Thailand*

การตรวจหาสารตกค้างจำพวกคลอรีนไฮโดรคาร์บอนในปลาดุก กุ้ง น้ำแม่น้ำ และตะกอนดินจากแหล่งกำเนิดธรรมชาติในประเทศไทย

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บทคัดย่อ : **ดานิศ ทวีติยานนท์, วรา พานิชเกรียงไกร, สุพัตรา ศรีไชยรัตน์, ประภัสสรา พิมพันธ์ และสุนันทา เวศอุไร. 2535. การตรวจหาสารตกค้างจำพวกคลอรีนไฮโดรคาร์บอนในปลาดุก กุ้ง น้ำแม่น้ำ และตะกอนดินจากแหล่งกำเนิดธรรมชาติในประเทศไทย. วารสารวิจัยวิทยาศาสตร์การแพทย์ 6(2) : 97-116**

ทำการตรวจหาสารเคมีกำจัดศัตรูพืชชนิดออแกโนคลอรีน โดยวิธีแกสโครมาโตฟราฟฟี จำนวน 11 ชนิดจากตัวอย่างน้ำแม่น้ำ, ตะกอนดิน, ปลาดุกด้าน และกุ้ง จากแม่น้ำสายสำคัญของจังหวัดอุบลราชธานีและสุพรรณบุรี ในปี พ.ศ. 2533 ผลที่ได้จากทั้งสองจังหวัดมีความคล้ายคลึงกัน โดยที่ไม่มีความสัมพันธ์กันของปริมาณสารเคมีกำจัดศัตรูพืชในตัวอย่างที่ทำการตรวจ ตัวอย่างน้ำเกือบทุกตัวอย่างพบแต่ยาฆ่าแมลงดีลดรินและอัลดริน ตัวอย่างตะกอนดินจากทั้งสองจังหวัดมีการปนเปื้อนของยาฆ่าแมลงหลายชนิด โดยมีความเข้มข้นสูงสุดในจังหวัดอุบลราชธานี และสุพรรณบุรีเท่ากับ 0.233 และ 0.012 มก.ต่อกก.ตามลำดับ ในปลาดุกด้าน และกุ้งมีการปนเปื้อนของสารเคมีดังกล่าวบ้างเล็กน้อย ถึงแม้ว่าในบางพื้นที่ของทั้งสองจังหวัดมีการปนเปื้อนของสารเคมีกำจัดศัตรูพืชชนิดออแกโนคลอรีนค่อนข้างสูง โดยทั่วไปแล้วคุณภาพของน้ำ และอาหารที่ได้จากสัตว์น้ำ เช่น ปลาดุกและกุ้ง ยังคงอยู่ในระดับที่ยังยอมรับได้ว่าปลอดภัยจากสารเคมีชนิดออแกโนคลอรีน

คำสำคัญ : *ยาฆ่าแมลงจำพวกออแกโนคลอรีน; สารตกค้างในปลาดุก กุ้ง น้ำแม่น้ำ และตะกอนดิน*

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Abstract : **Danis Davitiyananda, Wara Panichkringkrai, Supatra Srichairat, Prapasara Pimpun, and Sunantha Vesaurai. 1992. Detection of chlorinated hydrocarbon residues in catfish, shrimp, river water and sedimentation from natural source in Thailand. Thai J Hlth Resch 6(2): 97-116**

Eleven organochlorine pesticides were determined by electron capture gas chromatography in river water, soil sediment, catfish and shrimp samples collected from different areas of the main rivers in Ubon Ratchathani and Suphan Buri provinces. Similar results were obtained from the two provinces. There were no relationship of pesticides concentraion between the samples investigated. Dieldrin and aldrin were the most commonly found in every river water samples. Detectable amounts of various organochlorine pesticides in soil sediment with maximum concentration of 0.233 mg/kg and 0.012 mg/kg in Ubon Ratchathani and Suphan Buri respectively. Traces of various organochlorine pesticides were also identified and detected in catfish and shrimp samples. High contamination of the pesticides were found in some areas in which many pesticides have been frequently used. However, the result from this study indicated that the quality of water and food from aquatic animals such as catfish and shrimp are still acceptable.

Key words : *Insecticide, organochlorine; Residues, catfish, shrimp, river water, soil sediment.*

Introduction

Nowadays there are more problems concerning toxic substances all over the world especially in the developing countries like Thailand. Farmers used more insecticides to increase agricultural productions with not enough consideration of the harmful effects. Furthermore, there are problems from factories and the use of various toxic substances as household insecticides.

During the past two decades, there are reports about environmental pollution in Thailand. Especially in the rivers and canals where aquatic animal belong as the source of proteins. Besides, qualities of drinking water in the main rivers such as Chaopraya River, Thachin River, Maeklong River, and Bangpakong River have become worse (Boonlong *et al.*, 1989). This includes the Gulf of Thailand, the eastern sea coast where there are plenty of various toxic substances as in those rivers. There are heavy metals, fertilizers, pesticides and insecticides. During B.E. 2521-2531 (1978-1988), there were reports from the office of the National Environmental Authority that 4,000 water samples from 48 rivers in Thailand contained various toxic substances such as lead, cadmium, mercury, arsenic, insecticides for instance aldrin, dieldrin, DDT, heptachlor, heptachlor M-oxide, Mirex, B.H.C. and lindane.

In B.E. 2525 (1982) there were insecticides found in half of the 1,500 water samples and from 1,300 soil and sedimentation samples. In 1984, there were organochlorine insecticides found as high as 52% out of 462 Thachin River water samples. Some of these contained toxic substances much higher than the set standards.

The finding of polluted river raised the question of whether the aquatic animals in this water can be safely consumed. These aquatic animals are unexpensive sources of protein compared with other animals. Native styles of fishing is still an important way to supply food protein. Though the raising of fish become more industrialization but for local people the rivers and canals are still important sources of fish and aquatic animals.

The research in set for 2 provinces namely Ubon Ratchathani in the northeast and Suphan Buri in the west of Thailand.

Ubon Ratchathani is a big province near the border in the northeast with many important rivers such as Khong river, Chee river, Mool river, Lam Dome Noi and Lam Dom Yai, there are several big and small lakes distributed over the province. People here are mainly farmers who grow glutious rice and other crops such as tapioca, jute, peanut as well as corn for animal feeds (Statistical reports of Changwat Ubon Ratchathani, 2531) and who are certainly assumed to use pesticides for agriculture.

Suphan Buri province is an important province in the west of Thailand. According to provincial statistics of Suphan Buri (2531). Thachin river or Suphan Buri river is the main water source for people here who are mainly farmers concentrating in growing rice, vegetables and fruits along with fresh water fishing.

Even though there are no exact statistics to confirm the use of pesticides in the above 2 provinces, it can be certain that wherever there are planting and animal raising there are pesticides used. According to the records of pesticides sold in Thailand in B.E. 2531. (Pudhiprechapong, 1988), 48,803 tons were sold with the value above 5,000 millions baths. These numbers were divided into 23,425 tons with value of 2,000 million baths for herbicides, 16,374 tons with value of 1,993 million baths for insecticides.

The objective of this research is to find the residues of insecticides in catfish, shrimps, water and the soil sediment where these aquatic animals live in.

Meterials and Methods

Sampling

Water, soil sediment, catfish and shrimps were collected from the main river in Ubon Ratchathani province and Suphan Buri province during 2-8 July 1990 and 17-21 September 1990 respectively. The sample collection sites which are numbered according to the river flowing from upstream to downstream in Ubon Ratchathani and Suphan Buri provinces were showed in Figure 1, 2 and Table 1 respectively.

River water samples were stored in amber glass bottles. Soil sediment samples taken out from river bottom were kept in clean polyethylene bag. Shrimps and catfish were captured from each collection sites with seines or gill nets. Immediately after capture, the fish and shrimps were weighed and packed in clean polyethylene bag then freeze with dry ice and kept in cool boxes. Samples remained frozen until they were prepared for residue analysis by the method described in AOAC (1990).

Instruments and Reagents

Instruments

a) Gas chromatopraphy: Varian 740 gas chromatography equipped with ^{63}Ni electron capture detector and Varian 427a integrator. The following GC condition were set. Column: 2 m × 0.2 cm.id. glass column packed with 1.5% SP 2250 and 1.95% SP 2401 on 100-120 mesh Supelcon AW-DMCS. All column packings were well conditioned before used. The flow rate of carrier gas (purified nitrogen) was 30 ml per minute. Thermal parameter: column temperature, 200°C; injection temperature, 220°C and detector temperature, 250°C.

b) Soxhlet apparatus: Electromantle ME, Electrothermal Co.

c) Evaporator: Rotavapor (RE 120, Buechi) equipped with an Eyela Cool Ace (CA101, Tokyo Rikakika Co.Ltd.)

Reagents

All reagents used were analytical grade and were tested for the absence of substances causing detector response before used. All reagents were obtained from E.Merck. They were acetonitril, diethyl

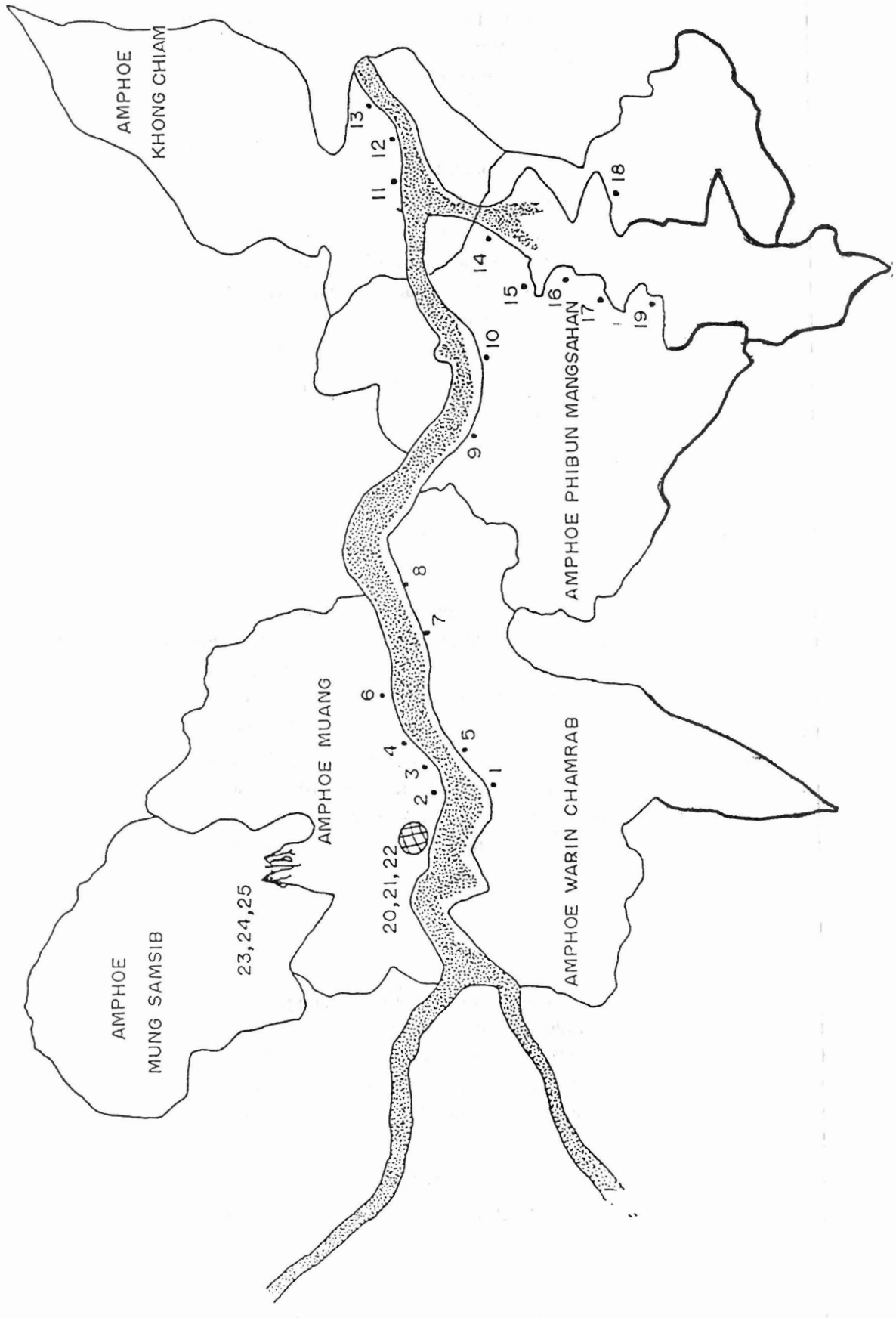

Figure 1 : Indication of area which catfish, shrimp, soil sediment and water samples were collected from Ubon Ratchathani province.

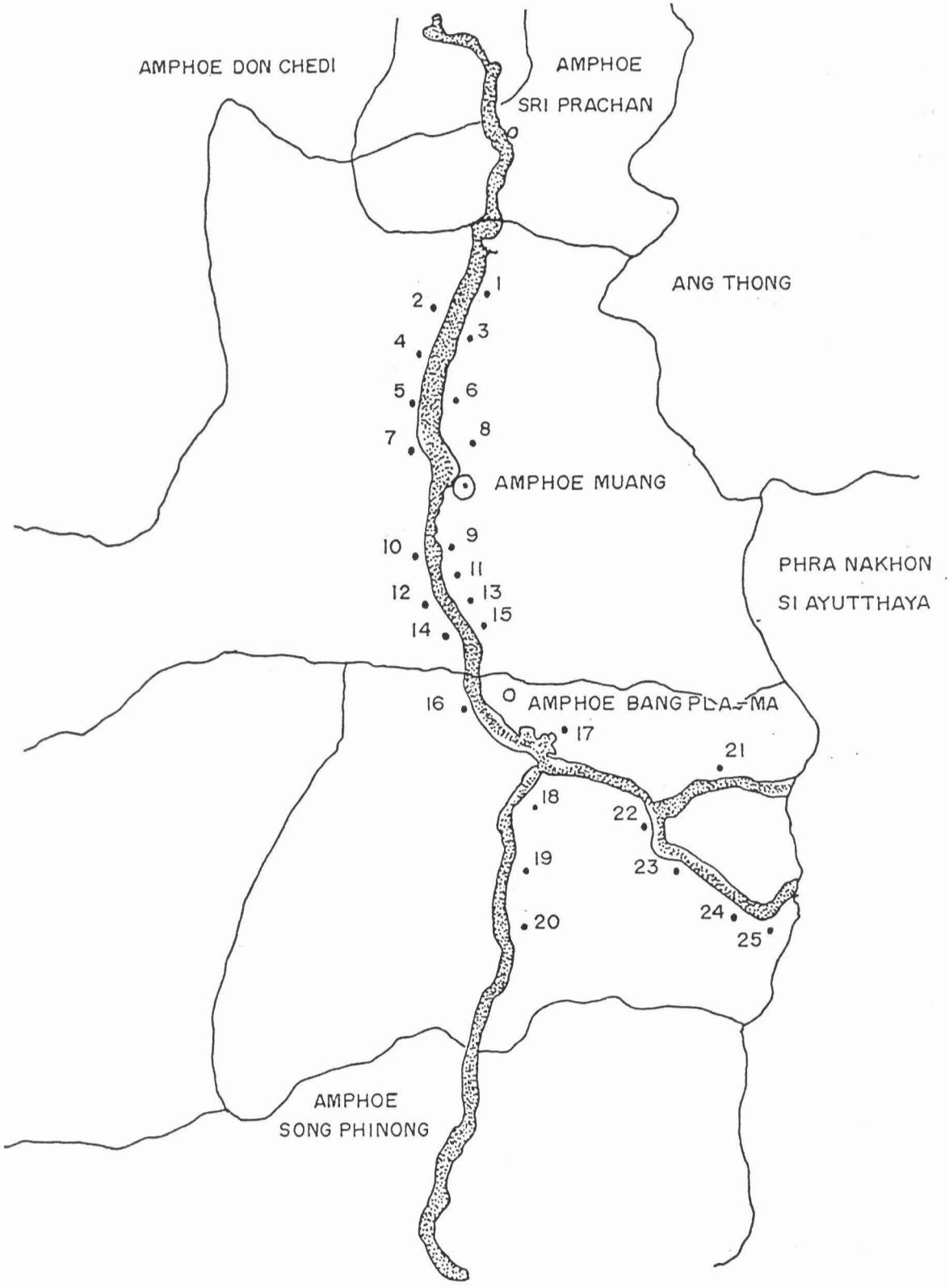

Figure 2 : Indication of area which catfish, shrimp, soil sediment and water samples were obtained from Suphan Buri province.

Table 1 : Name of the collection sites in Ubon Ratchathani and Suphan Buri Provinces

Collection site	Ubon Ratchathani		Suphan Buri	
	Ban	**Tambon**	**Ban**	**Tambon**
1	Had Suansuk	Kamnumsab	Ban Pihandaeng	Pihandaeng
2	Ta Wangtai	Nai Muang	Ban Mue 2	Po Paya
3	Rong Kasad	Nai Muang	Ban Mue 3	Po Paya
4	Bung Krangrueng	Nai Muang	Ban Watchisukkasem	Pihandaeng
5	Wang Kwanghung	Kamkwang	Man Huaweng	Ruayai
6	Gudlad	Gudlad	Ban Lau Tong	Sanamchai
7	Bung Malang	Bung Malang	Ban Mue 2	Ruayai
8	Bua Toeng	Ta Chang	Ban Mue 1	Sanamchai
9	Gang Sapue	Gang Sapue	Ban Huatanon	Ta piliang
10	Ban Hinlad	Gug Chompoo	Ban Kulie Tong	Ruayai
11	Ban Danmai 2	Khong Chiam	Ban Kokmor	Ta Rahad
12	Ban Danmai 1	Khong Chiam	Ban Watrast	Ta Piliang
13	Ban Danmai 3	Khong Chiam	Ban Mue 1	Ta Rahad
14	Kog Tiang	Kunrai	Ban Watmanau	Tab Teeleg
15	Ban Kamgom	Fangkam	Man Pokoi	Ta Rahad
16	Non Chig	Fangkam	Ban Kaohong	Bang Plama
17	Non Chan	Non Gor	Ban Kokkram	Kokkram
18	Bag Chum	Non Gor	Ban Taka Mue 1	Ban Taka
19	Nog Ten	Non Gor	Ban Chiprakao	Ban Taka
20	Ang Huaymueng 1	Nai Muang	Ban Laem	Ban Laem
21	Ang Huaymueng 2	Nai Muang	Ban Klongmong	Ongkarag
22	Ang Huaymuang 3	Nai Muang	Ban Ongkarag Mue 1	Ongkarag
23	Nong Changyai 1	Mueng Samsib	Ban Ongkarag Mue 7	Ongkarag
24	Nong Changyai 2	Mueng Samsib	Ban Paikongdin	Paikongdin
25	Nong Changyai 3	Mueng Samsib	Ban Bohuagroed	Paikongdin

ether, petroleum ether, florisil, n-hexane, chloroform, aluminium trioxide, anhydrous sodium sulphate and sodium chloride.

Sample Preparation

Catfish and Shrimp

Only edible portion of fishes and shrimps were separately removed and ground to paste. The 20 g of each sample was desicated in anhydrous Na_2SO_4 (ca. 50-100 g) and extracted with petroleum ether on soxhlet apparatus at 60°C for 6 hours. Extracted 3 times by partitioning each time with 30 ml saturated methyl cyanide and then 2 times with 650 ml distilled water, 40 ml saturated sodium chloride solution and 100 ml petroleum ether each time. Washed the extract twice with each time of 100 ml distilled water. Filtered the extract through anhydrous sodium sulphate and concentrated to ca 5 ml. The extract was then cleaned up with 5% Al_2O_3 column and eluted 6 times with 20 ml n-hexance. Reduced the volume of the eluate and adjusted to 5 ml with n-hexane.

Water

Extraction 800 ml of river water with 100 ml of n-hexane and then 2 times by each time with 50 ml n-hexane. Combined all the n-hexane layer and filtered through anhydrous sodium sulphate. The extract was vacuum evaporated to dryness and then redissolved in 5.0 ml of n-hexane.

Soil Sediment

The river soil sediment was dried at ambient temperature, pulverized and sieved through a 20 mesh sieve. Accurately weighed 50 g of samples and extracted organochlorine insecticides contained in soil sediment with 250 ml of chloroform on soxhlet apparatus at 60°C for 8 hours. Reduced the volume and clean-up through florisil column eluting first with 200 ml of 6% diethyl ether in petroleum ether and then with 200 ml of 16% diethyl ether in petroleum ether. The eluat was then vaccum evaporated to dryness and redissolved to 5 ml with n-hexane.

Organochlorine pesticides in the extracts were then quantitative analysed by electron capture gas chromatography.

Results

Ubon Ratchathani

The concentration of 11 organochlorine pesticides in river water, soil sediment, catfish and shrimp at each collection site is reported in Tab. 2, 3, 4 and 5 respectively. The areas which contained high level of organochlorine pesticides in samples are showed and characterized in symbols as shown in Fig. 3.

Only dieldrin was identified in most of the river water samples analyzed and the concentration was in the range of 0.01-0.09 ppb. There was only one sample from collection site no.18 contained o,p TDE but dieldrin was undetectable. Low concentration of aldrin was also found in river water samples from the collection sites 11 and 12.

Detectable amounts of various organochlorine pesticides in soil sediment were found in all collection sites as shown in Tab. 3. Collection sites 18, 23 and 25 contained considerable level of DDT and its metabolites. The total DDT concentration at the collection sites 18,23 and 25 were 0.128,0.56 and 0.233 ppm (mg/kg) respectively. Collection site 12 contained low level of DDT and its metabolites, but the highest concentration of endrin (0.027-ppm) was detected at the same area.Collection sites 23 and 25 contained high amount of total DDT and also having considerably amount of aldrin, dieldrin and heptachlor.

Traces of 11 organochlorine pesticides in catfishes were identified in all collection sites, with the most commonly found was DDT and its metabolites. Analysed results of pesticide residues are shown in Tab.4. Collection sites which had high level of insecticides concentration were 1,3,4,5,9,10,12,14,15,20,23 and 25. Considerably amount of dieldrin (≥ 0.010 ppm) were found only at the collection sites 4,9,14,15,20 and 25.

Table 2 : Concentrations of organochlorine pesticides in river water at different collection sites in Ubon Ratchathani

Pesticides	Collection sites /ppb																								
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
DDT(p,p')	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
DDT(o,p')	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
DDE(p,p')	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
TDE(p,p')	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
TDE(o,p')	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.050	0	0	0	0	0	0	0
Aldrin	0	0	0	0	0	0	0	0	0	0	0.001	0.010	0	0	0	0	0	0	0	0	0	0	0	0	0
Dieldrin	0.060	0.030	0.020	0.070	0.080	0.050	0.050	0.020	0.030	0.090	0.070	0.070	0.060	0.030	0.020	0.050	0.020	0	0.030	0.030	0.030	0.030	0.030	0.010	0.030
Endrin	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Lindane	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Heptachlor	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Heptachlor Epoxide	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Table 3 : Concentrations of organochlorine pesticides in soil sediment at different collection sites in Ubon Ratchathani

Pesticides	Collection sites /ppm																								
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
DDT(p,p')	0	0.007	0.001	0.002	0.001	0.001	0.002	0.003	0.002	0.002	0.003	0	0.001	0	0	0	0.002	0.033	0.006	0.001	0.006	0.001	0.004	0.001	0.034
DDT(o,p')	0	0	0.001	0.001	0	0.001	0	0.001	0	0	0.002	0	0	0	0	0	0.002	0.012	0.001	0	0.002	0	0	0	0
DDE(p,p')	0.001	0.002	0.001	0.002	0.001	0	0.001	0.001	0.003	0.001	0.004	0.004	0.001	0.001	0.002	0.002	0.002	0.025	0	0	0.002	0.003	0.052	0.001	0.108
TDE(p,p')	0	0	0.002	0.003	0.002	0.001	0	0.001	0.003	0.001	0.004	0	0	0	0.004	0.001	0.002	0.043	0.001	0.001	0.002	0.001	0	0.001	0.033
TDE(o,p')	0	0	0	0	0	0	0	0	0.002	0.002	0	0.003	0	0	0	0	0	0.015	0.002	0	0	0	0	0	0.058
Aldrin	0.004	0.001	0.003	0.006	0.004	0.002	0.001	0.001	0.009	0.001	0.004	0.002	0.005	0.002	0.001	0.001	0.003	0.003	0.001	0	0.002	0.007	0.673	0	0.195
Dieldrin	0.004	0.004	0.002	0.003	0.007	0.004	0.003	0.002	0.002	0.003	0.006	0.006	0.001	0.003	0.006	0.005	0.008	0.009	0.001	0.003	0.004	0.002	0.121	0.001	0.060
Endrin	0.002	0	0	0	0	0.002	0.001	0.001	0	0	0	0.027	0.001	0.001	0	0	0	0	0	0.002	0	0.001	0	0	0
Lindane	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0.001	0	0.001	0	0	0	0	0	0
Heptachlor	0.001	0	0.001	0	0.002	0	0	0	0	0	0.011	0.001	0.001	0.001	0	0.001	0.001	0.001	0.001	0	0	0.001	0.034	0.001	0.028
Heptachlor Epoxide	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Table 4 : Concentrations of organochlorine pesticides in catfishes at different collection sites in Ubon Ratchathani

Pesticides	Collection sites /ppm																								
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
DDT(p,p')	0.009	0.001	0.007	0.006	0.011	0.003	0.004	0.001	0.007	0.012	0.003	0.012	0.005	0.012	0.005	0.004	0.001	0.003	0	0.007	0.001	0.008	0.005	0.006	0.004
DDT(o,p')	0.009	0.001	0.002	0.001	0.009	0.001	0	0	0.004	0.011	0.001	0.003	0	0.006	0.007	0	0.002	0	0	0.004	0.001	0.001	0.002	0.001	0.001
DDE(p,p')	0.016	0.003	0.028	0.008	0.029	0.003	0.004	0.001	0.011	0.021	0.006	0.009	0.049	0.007	0.006	0.004	0.003	0.006	0.004	0.011	0.001	0.002	0.004	0	0.004
TDE(p,p')	0.007	0.003	0.005	0.004	0.010	0.002	0.005	0.001	0	0.009	0.001	0.004	0.001	0.008	0.004	0.005	0.001	0.003	0.005	0.005	0.002	0.001	0.009	0.002	0.003
TDE(o,p')	0.005	0	0.001	0	0.005	0.002	0	0.001	0	0.004	0	0.001	0	0.004	0.003	0	0	0	0	0	0.001	0	0	0.001	0
Aldrin	0.001	0.001	0	0.001	0.002	0.003	0.001	0.001	0.001	0.001	0.001	0.002	0	0.003	0.002	0.001	0.002	0	0.001	0.001	0	0	0.003	0.001	0.002
Dieldrin	0.009	0.006	0.004	0.015	0.009	0.005	0.004	0.004	0.066	0.007	0.006	0.006	0	0.010	0.010	0.003	0.005	0.005	0.003	0.066	0.003	0.006	0.007	0.006	0.036
Endrin	0.002	0.001	0	0.002	0.001	0.003	0	0.001	0	0.003	0	0.002	0	0	0.004	0	0	0	0	0	0	0	0.001	0.003	0.001
Lindane	0	0	0	0	0.001	0.001	0.001	0	0	0	0	0	0	0.001	0.001	0	0	0	0	0	0	0	0	0.001	0.001
Heptachlor	0.001	0.001	0.001	0	0.001	0.001	0	0.001	0	0.001	0	0	0.002	0.001	0.002	0.001	0	0	0	0	0	0	0	0	0
Heptachlor Epoxide	0	0	0.002	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Table 5 : Concentrations of organochlorine pesticides in shrimps at different collection sites in Ubon Ratchathani

Pesticides	Collection sites /ppm																								
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
DDT(p,p')	0.005	0.003	0.004	0.001	0.001	0.001	0.003	0.002	0.001	0.001	NS	0.013	NS	NS	0.003	0	NS	0	NS	0.002	NS	NS	0.001	0.002	0.003
DDT(o,p')	0.001	0.001	0	0	0	0	0	0	0	0	NS	0.003	NS	NS	0	0	NS	0	NS	0.002	NS	NS	0	0	0
DDE(p,p')	0.008	0.005	0.005	0.001	0.005	0.002	0.003	0.001	0.001	0	NS	0.002	NS	NS	0	0	NS	0	NS	0.001	NS	NS	0.001	0	0.001
TDE(p,p')	0.007	0.002	0.001	0	0	0	0.001	0	0.001	0	NS	0.015	NS	NS	0.001	0	NS	0	NS	0	NS	NS	0	0	0
TDE(o,p')	0	0	0	0	0	0	0	0	0.001	0	NS	0.003	NS	NS	0	0	NS	0	NS	0	NS	NS	0	0	0
Aldrin	0.003	0.001	0.004	0	0	0	0.002	0.002	0.001	0	NS	0.002	NS	NS	0	0.002	NS	0	NS	0	NS	NS	0	0.002	0.004
Dieldrin	0.013	0.004	0.013	0.007	0.008	0.011	0.007	0.005	0.003	0.009	NS	0.007	NS	NS	0.019	0.016	NS	0.014	NS	0.006	NS	NS	0.005	0.007	0.001
Endrin	0	0	0	0	0.002	0	0	0	0	0	NS	0.001	NS	NS	0.001	0.001	NS	0.001	NS	0	NS	NS	0	0.002	0.001
Lindane	0.001	0	0	0	0.001	0	0.001	0.001	0.001	0	NS	0.001	NS	NS	0.001	0.001	NS	0.001	NS	0	NS	NS	0	0	0.001
Heptachlor	0.002	0.010	0.001	0	0	0.001	0.001	0	0	0	NS	0	NS	NS	0.001	0.001	NS	0.001	NS	0	NS	NS	0	0	0
Heptachlor Epoxide	0	0.001	0	0	0.001	0	0	0.001	0	0	NS	0	NS	NS	0	0	NS	0	NS	0	NS	NS	0	0	0

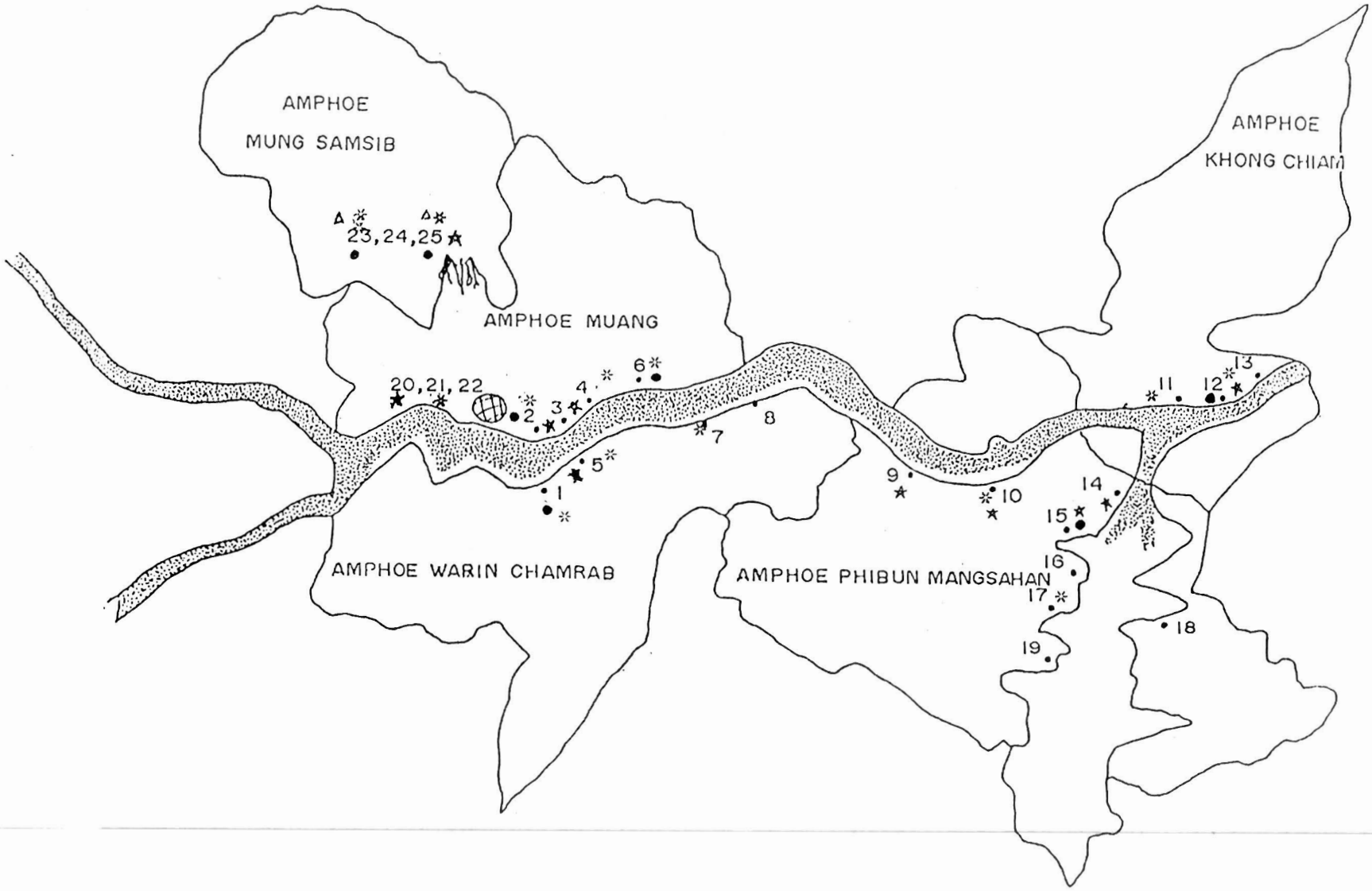

Figure 3 : Areas which found high contamination of organochlorine pesticide residues in Ubon Ratchathani characterized by symbols *, Δ ☆ and ● for water, soil sediment, catfish and shrimp respectively.

Detectable amount of organochlorine pesticides in shrimps were also found in all samples collected. High contamination of DDT and its metabolites and dieldrin were found at the collection sites 1,3,6,12,15,16 and 18.

There were no relationship of insecticides concentration between the sample groups investigated.

Suphan Buri

The results obtained from SuphanBuri are shown in Tab. 6,7,8 and 9. Most of samples collected from Suphan Buri river were contaminated with organochlorine pesticides, DDT and its metabolites and dieldrin. Fig. 4 shows the collection sites containing high pesticides concentration.

Traces of dieldrin and its metabolite product, aldrin were found in river water at all collection sites. No DDT and its metabolites were found. Collection sites 5 and 15 contained considerably amount of dieldrin and aldrin.

Soil sediment at all collection sites were identified for 11 organochlorine pesticides and were found ranging from 0 to 0.012 ppm. Substantially higher contamination of DDT and its metabolites calculated as total DDT were found at the collection sites 5,6,7,9 and 16 (Fig. 4). Collection sites 1 and 19 had low amount of total DDT and dieldrin, but contamination of more than 0.01 ppm of heptachlor were found. Considerably concentration of dieldrin was found at the collection sites 8 and 24.

Ten of the organochlorine pesticides residues in catfish samples were identified as shown in Tab. 8. Considerably amount of total DDT were found at the most collection sites. The concentration of organochlorine residues in catfish in each collection site varied from 0 to 0.021 ppm. Collection sites 2,4,13,-15 and 25 contained also high amount of total DDT and dieldrin.

As shown in Tab. 9, shrimp collected from SuphanBuri contaminated with small amount of DDT and its metabolites. More than 0.01 ppm of dieldrin were found at the collection sites 1, 5, 7, 10, 12, 17, 19, 21 and 24.

There were no relationship of organochlorine pesticides concentration between the sample groups analysed.

Discussion

The analysis results of samples collected from the Moon river during July 1990 were similar to those obtained from Suphan Buri river during the same year. DDt and its metabolites as well as dieldrin and aldrin were the most commonly found in every samples investigated. Dieldrin and aldrin accounted for the majority of residues detected in water. Some aldrin was converted to dieldrin, possibly by the action of atmosphere oxygen (WHO, 1979). Thus, some dieldrin found in water and other samples may be also the metabolic product of aldrin. It is well established that the organochlorines have a strong tendency to adsorb on surfaces. Most of them that enters water is already firmly attached to soil particles, and remain attached. It was shown that, if DDT does find its way into clear water, it is gradually lost by adsorption on surfaces. The data obtained from the two provinces showed also that many forms of organochlorine pesticides attached in soil sediment. Concentration in living organisms such as catfishes which habitual living around the river bottom may be involved with adsorption from soil sediment and water or by dissolution within their nonpolar constituents. However, the present study showed that, there was no relationship between organochlorines concentration in catfishes and soil sediment. One possible reason which migh explain this observation is that fishes were not living around there but swam from another area.

Anyhow, the organochlorine residues found in edible part of fish and shrimp samples, collecting from the two provinces, were not higher than the allowable level (≤ 0.1 mg/kg) which recommended by the Thai Ministry of Public Health (1982) for aquatic animals. There were some collection sites such as sites 23, 24 and 25 which located at Ampur Muang Samsib of Ubon Ratchathani had considerably high level of

Table 6 : Concentrations of organochlorine pesticides in river water at different collection sites in Suphan Buri

Pesticides	Collection sites /ppb																								
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
DDT(p,p')	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
DDT(o,p')	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
DDE(p,p')	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
TDE(p,p')	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
TDE(o,p')	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Aldrin	0.020	0	0.020	0.030	0.060	0.060	0.020	0.030	0.020	0.020	0.030	0.010	0	0	0.090	0	0.010	0.020	0.010	0.010	0	0	0	0.030	0.010
Dieldrin	0.060	0.050	0.010	0.060	0.130	0.003	0.070	0.070	0.050	0.070	0.070	0.020	0.060	0.010	0.030	0.060	0.010	0.060	0.010	0.010	0.010	0.080	0.070	0.080	0.010
Endrin	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Lindane	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Heptachlor	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Heptachlor Epoxide	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Table 7 : Concentrations of organochlorine pesticides in soil sedinent at different collection sites in Suphan Buri.

Pesticides	Collection sites /ppm																								
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
DDT(p,p')	0.004	0.004	0.004	0.002	0.003	0.012	0.002	0.004	0.010	0.003	0.007	0.006	0.004	0.004	0.004	0.005	0.007	0.003	0.003	0.001	0.002	0.001	0.002	0.001	0.001
DDT(o,p')	0	0	0.003	0.001	0.004	0	0.005	0	0	0.002	0.002	0	0	0	0	0.006	0	0.002	0	0.001	0.001	0	0.002	0	0
DDE(p,p')	0.002	0	0.003	0.002	0.011	0.004	0.010	0.001	0.004	0.004	0.006	0.003	0.005	0.005	0.001	0.011	0.001	0.004	0.001	0	0.001	0.001	0.004	0	0
TDE(p,p')	0	0	0.003	0.002	0.006	0.004	0.005	0.002	0.010	0.003	0	0.006	0.002	0.005	0	0.007	0	0.002	0.001	0.001	0.003	0.001	0	0	0
TDE(o,p')	0	0	0	0.003	0.007	0	0	0	0	0	0	0	0	0	0	0.009	0	0	0	0	0	0	0	0	0
Aldrin	0	0.001	0.002	0.002	0	0.002	0.004	0.001	0.002	0.002	0.001	0.001	0.002	0.003	0.004	0.002	0.002	0.002	0	0.001	0	0.001	0.001	0.001	0.002
Dieldrin	0.003	0.007	0.008	0.001	0.003	0.003	0.009	0.011	0.008	0.005	0.004	0.006	0.007	0.007	0.004	0.009	0.002	0.005	0.007	0.004	0.003	0.008	0.006	0.012	0.008
Endrin	0.001	0	0.003	0.001	0	0.002	0.002	0	0	0.002	0	0	0	0	0	0.004	0	0.002	0.003	0.001	0	0	0	0	0
Lindane	0	0	0	0	0.001	0	0.007	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Heptachlor	0.010	0.001	0.001	0.002	0	0	0.003	0	0.002	0.001	0.001	0	0.001	0	0.002	0.001	0.002	0.003	0.009	0.001	0.001	0.001	0	0	0
Heptachlor Epoxide	0	0	0	0.001	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Table 8 : Concentrations of organochlorine pesticides in catfishes at different collection sites in Suphan Buri.

Pesticides	Collection sites /ppm																								
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
DDT(p,p')	NS	0.008	0.010	0.006	0.008	0.007	0.005	0.009	0.008	0.002	0.001	0.006	0.008	0.001	0.004	0.003	0.002	0.002	0.010	0.003	0.009	0.004	0.010	0.003	0.006
DDT(o,p')	NS	0.008	0	0.010	0.006	0	0.007	0	0	0	0	0	0	0	0	0	0.003	0.001	0.004	0.001	0.016	0.005	0.012	0.001	0.004
DDE(p,p')	NS	0.001	0.021	0.020	0.013	0.013	0.008	0.012	0.016	0.035	0.030	0.007	0.013	0.003	0.012	0.002	0.001	0.004	0.009	0.003	0.009	0.004	0.008	0.003	0.004
TDE(p,p')	NS	0.008	0	0.011	0.017	0.008	0.006	0.010	0.008	0	0.001	0.006	0.011	0.001	0.008	0	0.003	0.001	0.009	0.001	0.006	0.004	0.004	0.001	0.004
TDE(o,p')	NS	0.004	0.007	0.004	0.004	0.003	0.006	0.003	0.004	0	0	0.003	0.002	0	0.002	0	0	0	0.003	0	0.003	0	0.005	0	0
Aldrin	NS	0.002	0.001	0.003	0.003	0.002	0.001	0.003	0.002	0.002	0.002	0.004	0	0.002	0.001	0.002	0	0	0.001	0.002	0.004	0.003	0.001	0	0.002
Dieldrin	NS	0.021	0.009	0.013	0.008	0.006	0.005	0.008	0.007	0.008	0.009	0.006	0.016	0.009	0.014	0.004	0.004	0.002	0.005	0.004	0.009	0.003	0.006	0.006	0.011
Endrin	NS	0.020	0	0.003	0	0.002	0	0	0.001	0	0.002	0.001	0.003	0.002	0.003	0	0.002	0	0	0	0.003	0	0	0.003	0.009
Lindane	NS	0	0.002	0.002	0.002	0.002	0	0.001	0.002	0.001	0.001	0.003	0.002	0.001	0.002	0.001	0	0.001	0.001	0.001	0.002	0.002	0	0	0.001
Heptachlor	NS	0.001	0.003	0.003	0.002	0.002	0.004	0.002	0.002	0.002	0.002	0	0.004	0.002	0.004	0.002	0.001	0.001	0.001	0.002	0.003	0.002	0.001	0.001	0.002
Heptachlor Epoxide	NS	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

Table 9 : Concentrations of organochlorine pesticides in shrimps at different collection sites in Suphan Buri.

Pesticides	Collection sites /ppm																								
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
DDT(p,p')	0.001	0	0.001	NS	0.002	NS	0.003	0.003	0.003	0	0	0.003	0.003	0.001	NS	NS	NS	NS	0.003	NS	0.002	0.005	0	0.006	0.002
DDT(o,p')	0	0	0	NS	0.002	NS	0.001	0.001	0.002	0	0	0.005	0.001	0	NS	NS	NS	NS	0	NS	0	0.001	0.001	0.004	0
DDE(p,p')	0.002	0	0	NS	0.002	NS	0.001	0.001	0	0.001	0	0.003	0.001	0.003	NS	NS	NS	NS	0.002	NS	0.004	0.004	0.002	0.007	0.007
TDE(p,p')	0	0	0	NS	0.001	NS	0	0	0.003	0	0	0.003	0	0.001	NS	NS	NS	NS	0	NS	0	0.002	0.004	0.004	0
TDE(o,p')	0	0	0	NS	0	NS	0	0	0	0	0	0	0	0	NS	NS	NS	NS	0	NS	0	0	0	0	0
Aldrin	0.003	0	0.001	NS	0.002	NS	0.002	0.001	0.002	0	0.003	0.003	0.002	0	NS	NS	NS	NS	0.004	NS	0.002	0.003	0	0.002	0.003
Dieldrin	0.010	0.006	0.004	NS	0.012	NS	0.018	0.008	0.005	0.015	0	0.031	0.008	0.009	NS	NS	NS	NS	0.016	NS	0.010	0.017	0.004	0.020	0.009
Endrin	0.001	0	0	NS	0.002	NS	0.001	0.001	0.002	0	0	0.003	0.001	0.002	NS	NS	NS	NS	0.001	NS	0.002	0.001	0	0	0
Lindane	0.003	0	0.001	NS	0.001	NS	0.001	0.001	0.001	0	0	0.002	0.002	0.001	NS	NS	NS	NS	0.002	NS	0.002	0.002	0	0.002	0.002
Heptachlor	0.001	0	0.001	NS	0.002	NS	0.001	0.002	0.002	0	0	0.003	0.002	0.002	NS	NS	NS	NS	0.002	NS	0.003	0.002	0	0.001	0.003
Heptachlor Epoxide	0	0	0	NS	0	NS	0.002	0	0	0	0	0.002	0	0	NS	NS	NS	NSA	0	NS	0.002	0	0	0	0

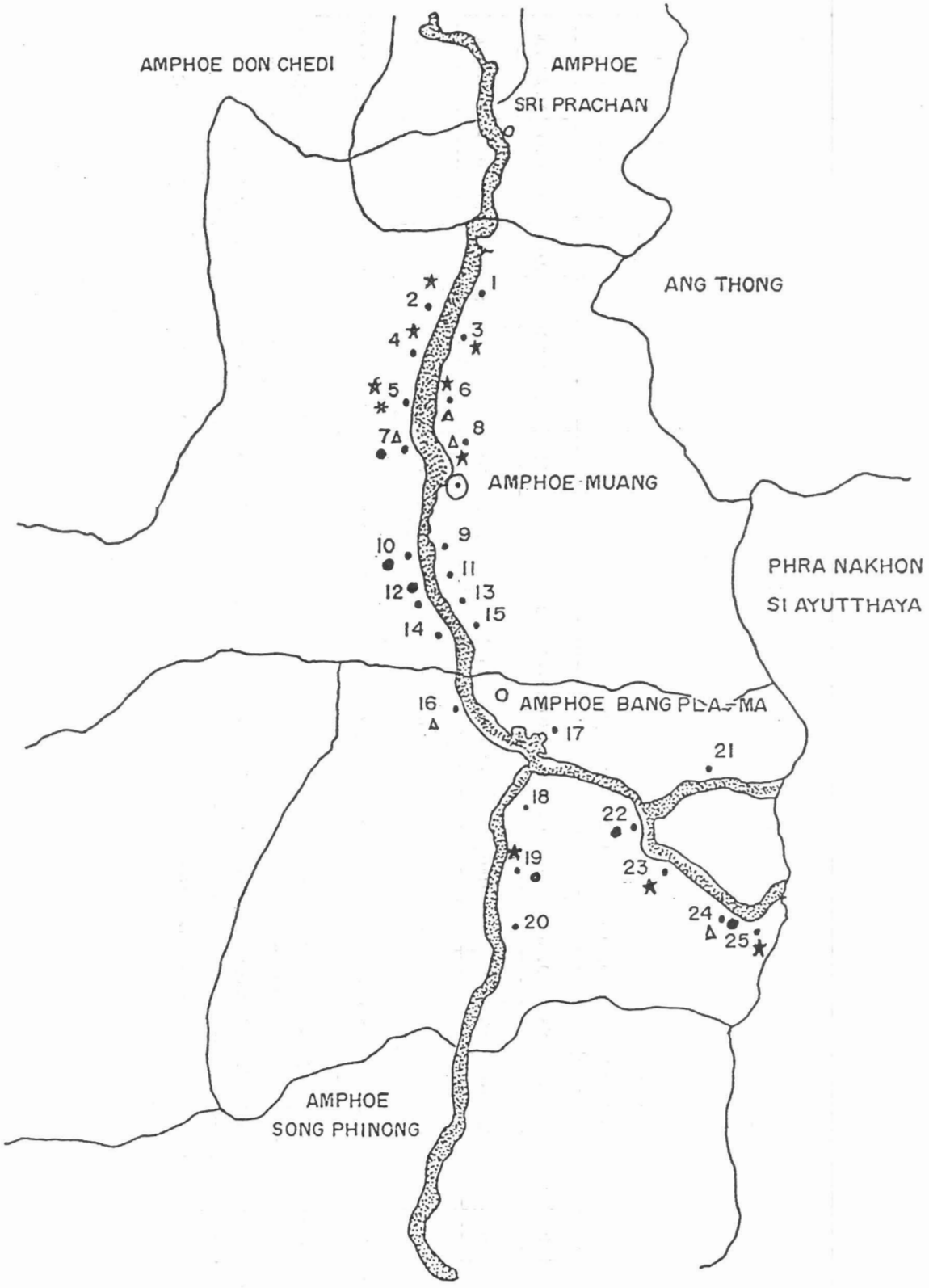

Figure 4 : Areas which found high contamination of organochlorine pesticide residues in Suphan Buri characterized by symbols *, Δ ☆ and ● for water, soil sediment, catfish and shrimp shrimp respectively.

pesticides in all samples investigated. These areas are used of chilli planting and many pesticides have been frequently used for controlling pests. Collection sites 9 and 20 in Ubon Ratchathani province and collection site 20 in Suphan Buri contained dieldrin in catfish more than 0.05 mg/kg. Comparing to the Acceptable Daily Intake limited by WHO in 1979 that the average intake of DDT from all source is unlikely to exceed 0.005 mg/kg/day. Thus, an adult with 70 kg body weight shoul not intake DDT from food and other sources more than 0.35 mg per day. There are, however, variation of the acceptable level of organochlorine residures permitted in foods obtained from fruits, meat and vegetables limited by the Ministry of Public Health in Thailand as showed in table 10.

Organochlorine insecticides are mainly DDT as well as its metabolic products, endrin, aldrin and dieldrin which are mostly found in investigated samples. They have been used for more than two decades in plant protection and DDT is used in malarial eradication in Thailand (Tayaputch, 1988). Until recently, their uses in agriculture have been limited but DDT is only one permitted for the malarial control. In despite of banning organochlorine substances some years ago in agricultural crop, their presence in the environment nowaday may be due to the persistence of cholinated pesticides, and with their wide spread used for malarial control in some area. These persistent organochlorine pesticides, at present, have been widely distributed in all agricultural areas even in rivers and canals and then accumulated in sediment and soil and end up in living organisms such as fish and other animals. With restriction of organochlorine application to livestock and forage crops, it is likely that there should be gradually decreased of their residues in environment and human food in the future. The results from this study indicated that quality of water, food from aquatic animals (catfishes and shrimps) from the two provinces are still safe from organochlorine pesticides.

Table 10 : Standard level of toxic residues permitted in foods.*

Toxic substances	Level of contamination (mg/kg)								
	Vegetables	Fruits	Grains	Dried beams	Fat & oil	Meat	Egg	Aquatic animals	Fresh milk
Aldrin	0.05	0.15	0.01	0.1	0.2	0.2	0.1	0.1	0.3
BHC	1.0	1.0	0.2	0.2	0.3	0.3	0.5	0.5	0.3
DDT	2.0	7.0	0.5	1.5	6.0	5.0	1.5	5.0	1.0
Dieldrin	0.1	0.1	0.02	0.1	0.1	0.2	0.1	0.3	0.3
Endrin	0.05	0.05	0.02	0.05	0.3	0.3	0.2	0.3	0.3
Heptachlor and Heptachlor epoxide	0.1	0.05	0.03	0.05	0.02	0.3	0.05	0.3	0.3

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