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Organochlorine Pesticide Residue Levels in Peninsular Malaysian Rivers

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Since the introduction of DDT as a pesticide in the late 1930s and the subsequent development of other organochlorine pesticides, the residues of these compounds have been found in many parts of the world (George *et al* 1966, Keith 1966, Hattula *et al* 1978, Pionke *et al* 1968). Their persistent and bioaccumulative properties in the aquatic environment have led to the discontinued usage of most of these organochlorine pesticides in the agricultural sector. The lipophilic nature and low chemical and biological degradation rates of many of these organochlorine pesticides lead to the accumulation of these compounds in biological tissues and subsequent magnification of concentrations in organisms progressing up the food chain (Mc Ewen *et al* 1979, Kennedy *et al* 1970, Moore et al 1964).

Malaysia is a country in which large areas of its land have been used for agriculture. Rubber and oil palm are two major plantation crops which occupy 3.8 million hectares covering 70% of the total agricultural land area. In addition to this, rice-growing is also an important agricultural activity contributing to nearly 60% of the country's supply of its annual rice consumption. The use of pesticides in the agricultural sector in Malaysia has been increasing over the years with some of the organochlorine pesticides such as lindane (γ-HCH), endosulfan and dieldrin still being permitted for use (Pesticides Board 1991).

An earlier study has been carried out to monitor the fate of these organochlorine pesticides with regard to the residue levels in water samples from two major rivers flowing through rice-growing areas on the west coast of Peninsular Malaysia (Tan 1992).

The present study was carried out to measure the extent of environmental contamination by these organochlorine pesticides in river waters from Peninsular Malaysia. Water samples were collected from different stations along 25 major rivers in Peninsular Malaysia (Figure 1) from 1990 to 1991.

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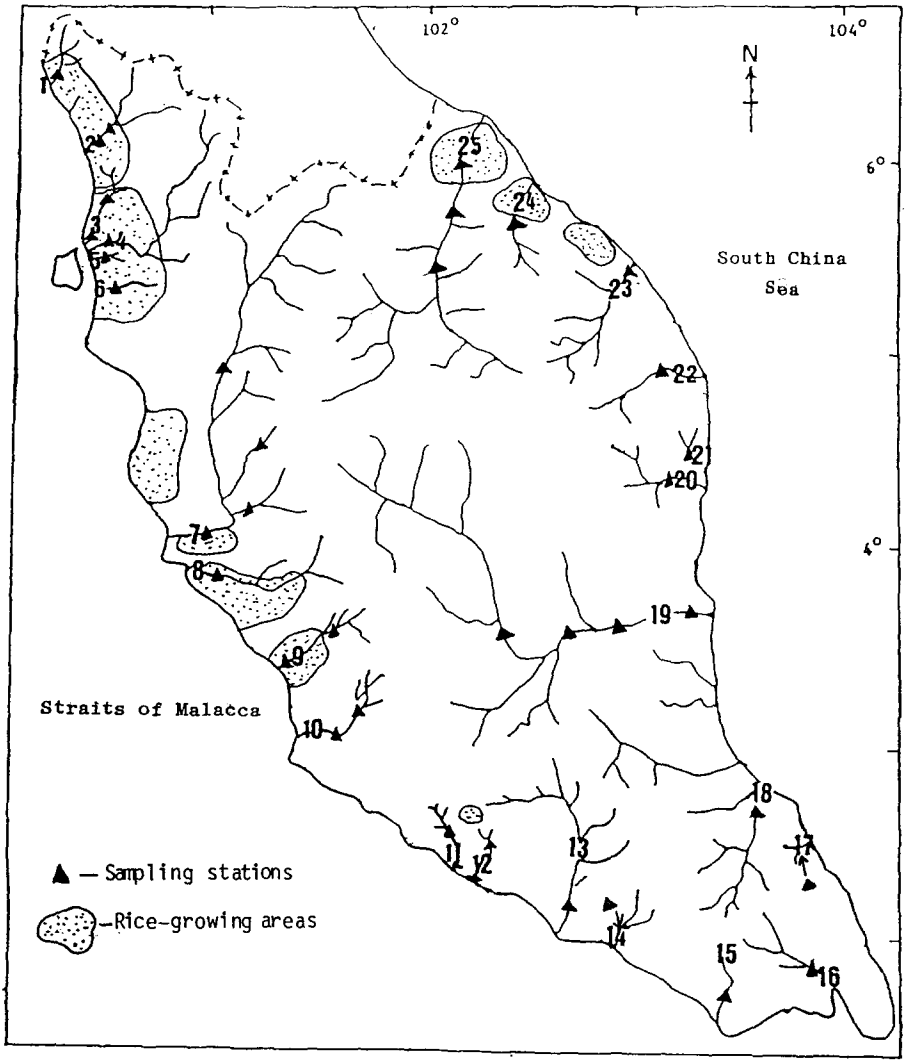

Figure 1: Major river basins of peninsular Malaysia.

MATERIALS AND METHODS

An Eyela rotary vacuum evaporator was used for concentrating the sample extracts. A Shimadzu GC 9A fitted with an electron capture detector (ECD) suitable for on-column injection and connected to a Shimadzu CR 3A integrator was employed for all gas chromatographic analysis in this study. Column : 2m x 3mm ID glass, coated with 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 mesh).

The use of high purity reagents and solvents helped to minimize interference problems. The impurity levels of all solvents and reagents used did not exceed an acceptable blank when subjected to the complete procedure without the sample. The solvents used in this study were obtained from various sources and were of different purities.

Standards - all organochlorine pesticide standards used in this study were obtained from USEPA, Cincinnati, Ohio. All standards came in a stock solution of 100 ug/mL of 99.8% purity. For calibration purposes, a portion of these stock solutions was diluted and a series of standard mixtures were prepared. All standard solutions/mixtures were stored in Teflon-lined screw capped amber bottles at 4°C. These solutions/mixtures were checked monthly for signs of degradation or evaporation. Standard mixtures were replaced after 3 months.

The grab sample technique was used whereby the water was collected from the river and filled into amber bottles. Water samples were collected in duplicates and were acidified to pH2 with sulfuric acid to eliminate biological activity in the water. The water samples were kept at ambient temperature (approx. 26-30°C) and then transported back to the laboratory for subsequent extraction and analysis. Prior to the solvent extraction procedure the water samples were also filtered to remove any suspended material or sediment.

All glassware in this procedure was washed with hexane. 250 mL of the river water sample was extracted with 3 x 8 mL of hexane. The extracts were combined and collected in a 250 mL round bottomed flask and concentrated using a rotary vacuum evaporator to about 10 mL for Florisil column chromatography clean-up.

Florisil column chromatography clean-up was used for fractionation of organochlorine pesticides from the water samples by elution with solvents of increasing polarity. The chromatographic columns (50cm x 15mm I.D) were slurry packed with 7g Florisil activated at 450°C overnight, made into a 1.5% v/w water/Florisil with distilled water and stirred for 3 hours before use. Approximately 0.5cm anhydrous sodium sulfate was placed at the top of the column to absorb any water in the sample or the solvent.

The column was pre-eluted with 60mL of petroleum ether. Just prior to the exposure of the sodium sulfate layer to the air, the washings from the flask containing the distilled off solvent was placed into the column and allowed to sink below the sodium sulfate layer. A total of 200mL petroleum ether was poured into the column and the eluate was collected in a round bottom flask. The elution was done with 5 different solvent mixtures, each a total of 200mL (100% pet. ether, pet. ether/ 6% diethyl ether, pet. ether/15% diethyl ether, 50% pet. ether/diethyl ether and 100% diethyl ether).

The eluates were then evaporated to dryness using a rotary vacuum evaporator and the residues were dissolved in 2 mL GC grade hexane for gas chromatographic analysis.

The separation and quantification of the pesticide residues were performed with the Shimadzu GC 9A fitted with an electron capture detector (ECD) using a mixed phase glass column (G.P. 1.5% SP-2250/1.95% SP-2401 on 100/120 Supelcoport, 2m x 3mm I.D.) which was purchased from Supelco Inc. The operating temperatures were: injector and detector, 250°C; oven temperature was maintained at 180°C for 13 minutes, then programmed at 5°C/min to 190°C and held there for 3 minutes before being raised to 200°C at the rate of 10°C/min and held at 200°C for 11 minutes. Nitrogen was used as the carrier gas at a flow rate of 50mL/min. The sample size was 2 ul.

The direct comparison technique using external standards was chosen for this study because the pesticides identified in the samples clearly matched known

organochlorine pesticide standards based on their retention times. The concentration of pesticide residues in the water was calculated using the formula.

$$C\ (ug/L) = \frac{W \times A_1 \times V_1}{A_2 \times V_2 \times V_3}$$

where

W : ng pesticide standard;
A_2 : peak area of standard
A_1 : peak area of sample;
V_2 : volume of extract injected, uL
V_1 : extract volume, mL;
V_3 : volume of sample extracted, mL

RESULTS AND DISCUSSION

An earlier study has shown that the recovery of these organochlorine pesticides from spiked reagent water and river water via solvent extraction with hexane followed by Florisil column chromatography clean-up exceeded 80% with minimum amount of standard deviation (Tan, 1992). Recovery from fortified samples of river water were: 93.0% for α-HCH; 97.0% for β-HCH; 95.0% for lindane; 103.0% for p,p'-DDE; 85.0% for p,p-DDT; 88.0% for heptachlor; 91.0% for endosulfan I; 93.0% for endosulfan II and 98.0% for dieldrin.

Hence this method for preconcentration of the organochlorine pesticide residues was adopted in the present survey.

Table 1 shows the analysis results of the organochlorine pesticide levels from water samples in 25 major rivers in Peninsular Malaysia. DDT and heptachlor were found in almost all the rivers. For the river systems flowing through major rice-growing areas - Sg. Merbok, Sg. Muda, Sg. Bernam, Sg. Selangor - the levels of t-DDT were substantially higher than those from the rivers along the east coast of Peninsular Malaysia - Sg. Kemaman, Sg. Kerteh, Sg. Dungun, Sg. Terengganu, Sg. Besut and Sg. Kelantan (see Figure 1). This could most probably be due to the fact that DDT was very widely used in these regions for the malarial eradication programme before its usage was discontinued and also to the fact that it is very highly stable with low degradeability.

The results for endosulfan also show a similar trend whereby the residue levels in water samples from rivers in the rice-growing areas - Sg. Perlis, Sg. Merbok, Sg. Muda, Sg. Perai, Sg. Bernam and Sg. Selangor - were all much higher than those from non rice-growing regions. For most of the rivers along the east coast of Peninsular Malaysia, the levels of endosulfan were not detectable. Endosulfan is still a widely used pesticide in the paddy fields for pest control.

These results for endosulfan in the rice-growing regions - Sg. Bernam and Sg. Selangor - have been confirmed from the monitoring studies carried out from June 1989 to July 1990 (Tan, 1992). The high levels of DDT and endosulfan in these rivers from the rice-growing areas have all exceeded the critical level of 4 ng/L and 10 ng/L, respectiveluy, as specified in the Malaysian Interim Standards for aquatic life (Goh et al, 1986).

Table 1 : Levels of organochlorine pesticides (OCPs) in peninsular Malaysian rivers

No.	River	Residue Levels(ng/L) t-HCH	t-Endo	Hept.	t-DDT	Dieldrin	Total OCPs
1.	Sg. Perlis	30	159	11	33	nd	233
2.	Sg. Kedah	50	25	16	42	11	144
3.	Sg. Merbok	32	111	15	35	15	207
4.	Sg. Muda	60	145	16	69	nd	290
5.	Sg. Perai	65	110	26	48	15	264
6.	Sg. Juru	54	47	18	52	nd	171
7.	Sg. Perak	9.4	1.3	5.3	25	2.8	44
8.	Sg. Bernam	320	62	120	190	39	731
9.	Sg. Selangor	280	310	100	110	47	847
10.	Sg. Klang	1.1	0.4	nd	9.5	4.0	15
11.	Sg. Linggi	2.7	nd	0.1	7.8	1.3	12
12.	Sg. Melaka	3.9	33	16	74	3.0	130
13.	Sg. Muar	nd	9.3	22	122	2.5	154
14.	Sg. Batu Pahat	nd	10	10	100	1.6	122
15.	Sg. Tebrau	1.4	1.0	29	59	14	104
16.	Sg. Johor	nd	13	11	65	34	123
17.	Sg. Mersing	4.0	47	10	88	2.6	152
18.	Sg. Pontian	7.7	12	13	44	8.8	85
19.	Sg. Pahang	0.9	nd	3.7	10	nd	15
20.	Sg. Kemaman	6.1	nd	4.0	0.3	nd	10
21.	Sg. Kerteh	2.3	nd	2.1	0.1	nd	5
22.	Sg. Dungun	0.3	nd	0.3	0.1	nd	1
23.	Sg. Terengganu	1.1	nd	1.0	0.2	nd	2
24.	Sg. Besut	0.2	nd	0.4	nd	nd	1
25.	Sg. Kelantan	0.5	nd	1.0	1.1	nd	3

nd = not detected (ie below detection limit); t-HCH = α-HCH + β-HCH + γ-HCH
t-DDT = p,p'-DDE + p,p'-DDT; t-Endo = endosulfan I + endosulfan II

Similarly the residue levels of HCH, dieldrin and heptachlor in Sg. Perlis, Sg. Kedah, Sg. Merbok, Sg. Muda, Sg. Perai, Sg. Bernam and Sg. Selangor have exceeded the critical levels for aquatic life.

From this study it is apparent that the ability for aquatic life such as fish to propagate in these rivers may be adversely affected by the presence of these organochlorine pesticide residues.

The present study shows that the continued usage of certain pesticides such as lindane (γ-HCH) and endosulfan in agriculture has been a contributing factor to the high levels in some river systems. Generally most of the other rivers in Peninsular Malaysia are still relatively free from organochlorine pesticide contamination especially those along the east coast (Table 1).

The results of this survey show that while the levels of organochlorine pesticides in most rivers are still tolerable in terms of quality for domestic use, some of those

rivers flowing through mainly rice-growing areas have exceeded the levels to maintain aquatic life.

A more extensive monitoring programme has been planned to confirm the present survey results. This will include the collection and analysis from sediment samples in the rivers.

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