

The Environmental Contamination by Organochlorine Insecticides of Some Agricultural Areas in Malaysia

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Abstract: Three agricultural areas including rice paddy cultivation (Muda) and vegetable farming (Cameron Highlands and Kundasang) were selected for studies on contamination by organochlorine insecticides. Both sediment and water samples were collected from these areas and analysed for 14 insecticides and their degradation products by the gas-chromatography mass-spectrometry (GC-MS) technique. The results showed that water samples from paddy fields contained significantly ($p \leq 0.01$) higher level of dieldrin when compared to those from vegetable farms. Endosulfan was found to be significantly higher ($p \leq 0.05$) in water samples from vegetable farming areas compared to paddy fields. All the 14 organochlorine compounds analysed were detected in sediments from both agricultural areas. While lindane was mostly found in sediments from paddy fields, DDT, DDD, endrin aldehyde and aldrin dominated in the sediments from vegetable farming areas. The concentration range of organochlorine insecticides and degradation compounds in water was mostly $< 1 \mu\text{g/L}$ whilst those found in sediment samples had a maximum value of $98 \mu\text{g/kg}$ (i.e. endrin).

Keywords: Organochlorine insecticides, vegetable farming, paddy fields, insecticide degradation products, GC-MS.

Abstrak: Tiga kawasan pertanian termasuk sawah padi (Muda) dan penanaman sayur-sayuran (Cameron Highlands dan Kundasang) telah dipilih untuk mengkaji status pencemaran oleh racun serangga jenis organoklorin. Sampel sedimen dan air telah dikutip daripada kawasan pertanian ini dan kandungan 14 jenis racun serangga organoklorin dan hasil degradasinya dianalisis dengan teknik kromatografi-gas spektrometri jisim. Keputusan menunjukkan bahawa sampel air dari kawasan padi mengandungi dieldrin yang lebih tinggi ($p \leq 0.01$) berbanding dengan air dari kawasan kebun sayur-sayuran. Manakala endosulfan didapati lebih tinggi ($p \leq 0.05$) dalam air dari kawasan penanaman sayur-sayuran berbanding kawasan padi. Semua jenis sebatian organoklorin yang dianalisis dapat dikesan dalam sampel sedimen dari kawasan pertanian yang dikaji. Lindan merupakan racun yang sering dijumpai dalam sedimen daripada kawasan padi manakala DDT, DDD, endrin aldehid dan aldrin merupakan racun yang utama dalam sedimen di kawasan kebun sayur-sayuran. Julat kepekatan sebatian organoklorin yang dianalisis dalam air ialah $< 1 \mu\text{g/L}$ dan dalam sedimen, kepekatan yang tertinggi dicerapi ialah $98 \mu\text{g/kg}$ untuk endrin.

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Introduction

Organochlorine insecticides are compounds that are not only toxic but also difficult to degrade under environmental conditions. The half-life of most organochlorine insecticides can range from several years to more than 10 years [1]. Because of their persistent behaviour, these insecticides, although present in trace quantity in the environment, can result in bioaccumulation. In view of the hazardous characteristics of these compounds, a number of them had been listed by the UNEP as persistent organic pollutants (POPs). Among them are aldrin, dieldrin, endrin, chlordane, DDT, heptachlor, hexachlorobenzene, mirex and toxaphene. These compounds have been assessed based on Decision 18/32, which was jointly initiated by the Inter-Organisation Programme for the South Management

of Chemicals (IOMC), International Programme on Chemical Safety (IPCS) and Intergovernmental Forum on Chemical Safety (IFCS) [1]. During the assessment, information regarding the toxicology, deposition and contamination of the environment, risks and benefit of usage, cost and strategies for eliminating discharge of these compounds were examined. On 22 May 2001, a total of 127 countries finally adopted the Stockholm Convention on POPs and ended the negotiation called for in 1997 by the Governing Council of UNEP on the need for urgent global action to protect human health and the environment from POPs. In view of this, data regarding environmental contamination by organochlorine compounds are particularly important.

In Malaysia, the usage of organochlorine insecticides listed as POPs are either prohibited or restricted. For example, aldrin, dieldrin, DDT, chlordane were all restricted in usage but after 1998, their usage had been discontinued. For heptachlor, hexachlorobenzene, mirex, toxaphene and endrin, they are never registered for use. Even though the usage of most POPs-listed organochlorine insecticides are prohibited, a number of studies on rivers and sediments throughout Malaysia demonstrated that most of these compounds are present in the aquatic environment [2-4]. In most of these studies, the sources of the contamination are not known.

One of the main sources of organochlorine insecticides is likely to be agricultural areas, especially the cultivation of vegetables and paddy. This is because these agricultural practices require intensive pest control over a short period of time. In this work, we have examined several agricultural areas in various parts of Malaysia for the presence of organochlorine insecticides. The aim is to identify the extent of contamination of POPs from agriculture activities in Malaysia apart from assessing their impact on the aquatic environment.

Experimental

The study areas included the Muda Scheme for paddy cultivation in Kedah (sampling points at M1 – M3, Figure 1), vegetable farming areas at Cameron Highlands in Pahang (sampling points at CH1 – CH5, Figure 2) and Kundasang Highlands in Sabah (Sampling points at SB1-SB4, Figure 3). At each agriculture area, sampling sites were selected along rivers that drained the area under study (Figures 1-3). Samplings were performed from April to August 1998. Both water and sediment samples were collected for the analysis of organochlorine insecticides. Several sediment samples were collected at each site using a grab-sampler to yield a composite sample representative of the site. The sediment sample was then wrapped in aluminum foil to prevent contamination. They were later frozen until analysis. Water samples were collected in glass bottles that were pre-extracted with hexane to prevent contamination. Once collected, the water samples were extracted as soon as possible with organic solvents according to USEPA procedures. The sample bottle was also extracted several times with extraction solvent to recover any organochlorine insecticides that were adsorbed onto the walls of the glass container.

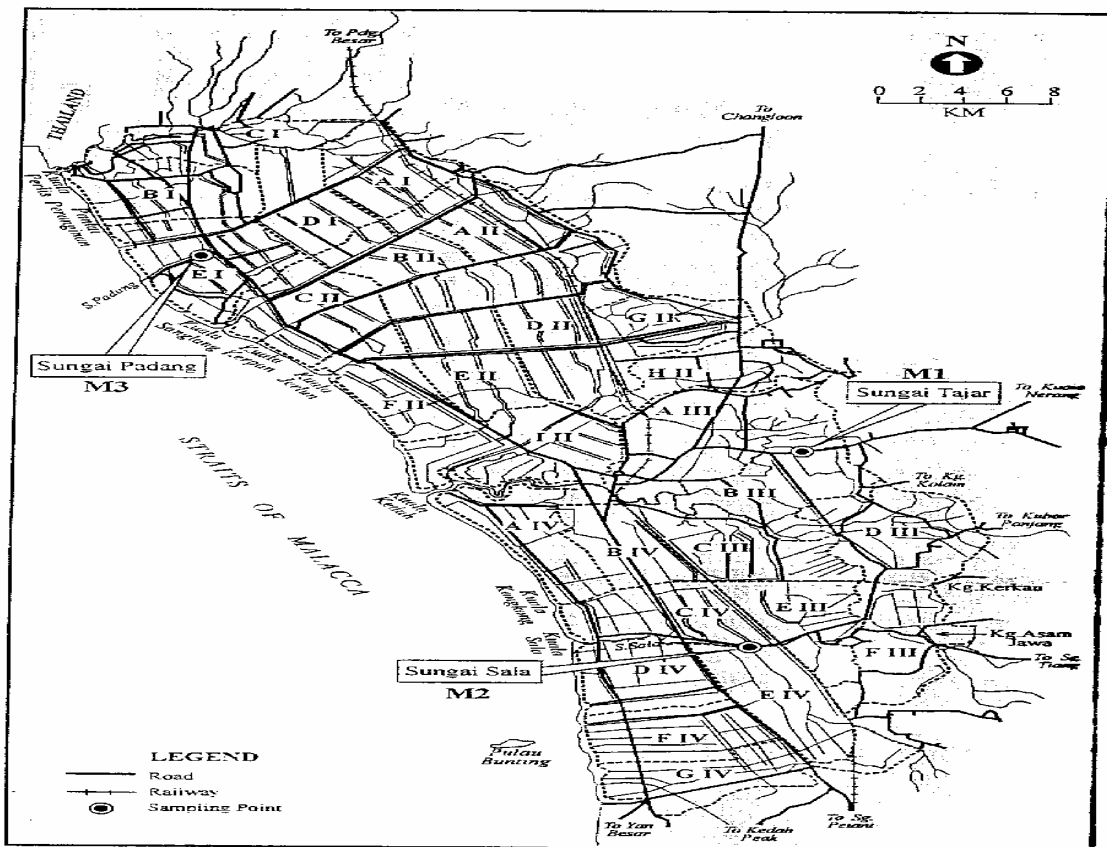


Figure 1: Locations (M) of sediment and water sampling at the Muda Scheme, Kedah

For extraction procedure before organochlorine analysis, 1 L of water was extracted using n-hexane as the extraction solvent (USEPA Method No. 3510). For sediment samples, 20 g of dried sediment was extracted by soxhlet extraction in a mixture of n-hexane:acetone (1:1 v/v) for 10 hours (USEPA Method No.3540). For the cleanup of extracts, USEPA Method No. 3620 was employed. This was carried out for both extracts from sediment and fish samples with florisil columns. The final extracts were then analyzed for organochlorine insecticides by gas-chromatography mass spectrometric (GC-MS) method. Qualitative identification of the organochlorine insecticides was based on retention times and comparison with reference mass spectrum. For quantitative determination of each compound, a calibration curve based on five pure standards of each organochlorine insecticide was constructed. ANOVA statistics was used to compare the differences in concentrations of insecticides. As for analytical quality control, 4,4-dibromobiphenyl was added in each standard and sample as internal standard. The GC-MS (Model GC-HP5980 and MS-HP5972) was operated in the Selected Ion Mode (SIM). The column used was SPB-608 and helium was used as the carrier gas. The list of insecticides analyzed, their quantifier ions and qualifier ions based on GC-MS is shown in Table 1.

Results and discussion

Organochlorine insecticides in water

Analysis of organochlorine insecticides in water or sediment yields different information regarding the existence of these compounds in the environment. The presence of organochlorines in water implies a

more recent input to the environment whilst their presence in the sediment indicates accumulation over a longer period of time. This is because of the lipophilic nature of this class of compounds, which have low solubility in water and their tendency to be adsorbed onto sediment, especially when the sediment contains high organic matter [5,6]. The level of organochlorine insecticides detected in the water from the Muda paddy fields, the Cameron and Kundasang vegetable farms are shown in Table 2.

It is obvious that, among all the organochlorine insecticides detected in the water samples, the BHC group is mostly absent except for the isomer γ -BHC (lindane) (Table 2).

In general, more types of organochlorine insecticides are found in water from vegetable farms than from paddy fields. Water samples from the Muda Scheme contained significantly higher level of dieldrin when compared to those from vegetable farms but the levels of endosulfan were higher in the water samples from the vegetable farms (Table 3).

Allowable levels of aldrin, BHC, t-DDT, endosulfan, heptachlor epoxide and lindane suggested by the Department of Environment for river water of Class II are 0.02, 2, 0.1, 10, 0.05 and 2 $\mu\text{g/L}$, respectively. Compared with these values, the water samples from the Cameron and Kundasang areas contained higher levels of t-DDT and aldrin than those allowed. Thus, vegetable cultivation areas such as Kundasang and Cameron were more contaminated by insecticide residues than paddy cultivation area like Muda. However, the levels of heptachlor epoxide in all three study areas have exceeded the suggested standard by 3 – 40 times with the Muda area particularly contaminated.

Insecticides	Quantifier Ions	Qualifier Ions
α -BHC	183	181, 109
β -BHC	183	181, 109
γ -BHC	183	181, 109
δ -BHC (Lindane)	183	181, 109
Heptachlor	100	272, 274
Heptachlor epoxide	353	355, 351
Aldrin	66	263, 220
Dieldrin	79	263, 279
4,4'-DDT	235	137, 165
4,4'-DDE	246	248, 176
4,4'-DDD	235	237, 165
Endosulfan I	195	339, 341
Endrin	263	82, 81
Endrin aldehyde	67	345, 250
4,4-Dibromobiphenyl (Internal standard)	152	312, 313

Table 1: Quantifier and qualifier ions of organochlorine pesticides used for the SIM of GC-MS

Insecticides	Muda		Cameron		Kundasang	
	Mean (10 ⁻³ µg/L)	Range	Mean (10 ⁻³ µg/L)	Range	Mean (10 ⁻³ µg/L)	Range
α-BHC	**ND		ND		ND	
β-BHC	ND		ND		ND	
γ-BHC	ND		62.08	(ND-113.6)	116.1	(ND-464.2)
δ-BHC	ND		ND		ND	
4,4-DDD	ND		42.16	(16.77-53.45)	ND	
4,4-DDE	ND		ND		ND	
4,4-DDT	ND		446.02	(442.0-450.7)	110.6	(ND-442.3)
Aldrin	19.06	(ND - 57.2)	484.4	(ND-1107.5)	35.68	(ND-59.9)
Dieldrin	409.5	(316.3 - 568.0)	118.5	(ND-172.8)	156.8	(125.2-199.8)
Endrin	ND		174.2	(ND-385.4)	46.55	(ND-118.8)
Endrin aldehyde	90.90	(65.60-133.7)	ND	ND	40.52	(ND-113.6)
Endosulfan I	42.73	(ND-128.2)	186.0	(47.8-260.0)	413.0	(236.9-718.3)
Heptachlor	ND		224.9	(ND-384.0)	ND	
Heptachlor epoxide	1858.7	(567.1-3606.0)	247.5	(ND-620.0)	167.1	(22.30-336.7)

** ND < 0.01 µg/L

Table 2 : The mean concentrations and ranges of organochlorine insecticides determined in water samples from rivers flowing through the Muda, Cameron and Kundasang agriculture areas.

Insecticides	Comparison (significant level)
Dieldrin	Muda > Cameron (***); Muda > Kundasang (***)
Endosulfan	Cameron > Muda (**); Kundasang > Muda (**)

** Significant difference at $p \leq 0.05$

*** Significant difference at $p \leq 0.01$

Table 3. Comparison of the levels of various insecticides in the water samples from agricultural areas studied.

Organochlorine insecticides in sediment

Unlike in water, all types of organochlorine insecticides and their degradation products that have been analyzed were detected in sediment samples (Table 4). This provides an indication of the usage of all these insecticides in the agriculture areas surveyed.

For the BHC insecticides, the sediment samples from the Muda paddy fields contained significantly higher concentration of lindane when compared to Kundasang vegetable farms (Table 5), but the levels

of 4,4-DDD and endrin aldehyde in the sediments of Cameron Highlands were higher than those from Muda areas (Table 5). The DDT concentration was also found to be very significantly higher in the sediments of Cameron Highlands when compared to that of Kundasang. Therefore, based on the levels of insecticides in sediment samples determined, it can be concluded that paddy cultivation areas are more contaminated by lindane whilst for vegetable farms, 4,4-DDD and endrin aldehyde.

Insecticides	Muda		Cameron		Kundasang	
	Mean ($\mu\text{g}/\text{kg}$)	Range	Mean ($\mu\text{g}/\text{kg}$)	Range	Mean ($\mu\text{g}/\text{kg}$)	Range
α -BHC	10.09	(8.31-12.04)	10.64	(4.01-21.51)	7.80	(6.38-9.80)
β -BHC	13.37	(4.6-21.34)	17.23	(5.55-37.43)	9.84	(5.40-14.23)
γ -BHC	21.95	(16.13-33.39)	9.71	(3.49-21.93)	7.80	(6.18-11.88)
δ -BHC	15.01	(3.70-25.42)	16.72	(5.90-32.93)	17.79	(9.50-25.74)
4,4-DDD	ND		34.2	(16.77-53.45)	17.02	(9.54-36.09)
4,4-DDE	ND		1.31	(0.43-2.18)	0.60	(ND-1.16)
4,4-DDT	ND		21.60	(21.13-22.63)	21.61	(18.80-26.33)
Aldrin	27.80	(**ND - 83.39)	17.39	(6.67-39.62)	58.59	(42.06-91.98)
Dieldrin	5.89	(ND - 15.31)	12.01	(6.50-19.70)	13.88	(7.94-27.54)
Endrin	33.19	(16.41-51.23)	46.58	(19.91-98.70)	41.70	(32.01-53.06)
Endrin aldehyde	3.25	(ND-9.74)	16.55	(6.81-25.96)	11.14	(5.63-11.72)
Endosulfan I	7.44	(3.00-13.28)	11.73	(1.54-25.48)	8.30	(ND-18.66)
Heptachlor	17.24	(ND-29.76)	16.55	(14.39-18.70)	20.74	(14.70-24.68)

** ND < 0.4 $\mu\text{g}/\text{kg}$

Table 4 : The mean concentrations and ranges of organochlorine insecticides in the sediment samples from the Muda, Cameron and Kundasang agriculture areas.

Insecticides (Sediment)	Comparison (significant level)
Lindane	Muda > Kundasang (**)
4,4-DDT	Cameron > Kundasang (***)
4,4-DDD	Cameron > Muda (**)
Endrin aldehyde	Cameron > Muda (**)
Aldrin	Kundasang > Cameron (**)

** Significant difference at $p \leq 0.05$

*** Significant difference at $p \leq 0.01$

Table 5 : Comparison of the levels of various insecticides in the sediment samples from agricultural areas studied.

Metabolites of organochlorine insecticides in water and sediment

The amount of degradation products (metabolites) of each insecticide when compared to the parent compound may give an indication of the frequency of the input of these substances to the environment and, to some extent, the rate of degradation of the parent compound. From Table 6, it is obvious that in water and sediment samples, 4,4-DDT has a significantly higher concentration than its degradation product 4,4-DDE or DDD, especially for

samples from the vegetable farms. This concentration distribution pattern may be attributed to possible continuous input and/or slow degradation of 4,4-DDT [1]. Endrin and aldrin were also found in significantly higher levels in sediment compared to their degradation products (Table 6). However, in water samples, aldrin was observed to be in lower concentration and this is probably due to a more rapid degradation of aldrin in the aqueous phase and also the less soluble nature of aldrin compared to dieldrin.

Insecticide	Muda	Cameron	Kundasang
Water samples			
Dieldrin > Aldrin	***		***
DDT>DDD		***	
Sediment samples			
DDT>DDE		***	***
Endrin> Endrin aldehyde	**	***	
Aldrin > Dieldrin			**

** - Significant difference at $p \leq 0.05$
*** - Significant difference at $p \leq 0.01$

Table 6 : Comparison of the concentrations of some organochlorine insecticides and their degradation products in the sediment and water samples of all agriculture areas studied.

Comparisons with other studies in Malaysia

The maximum levels of DDT, lindane, heptachlor, heptachlor epoxide, endosulfan, aldrin and dieldrin reported in the sediment of rivers from Sabah, East Malaysia were 73.6, 8.13, 17.6, 0.48, 1.34, 0.21 and 0.73 $\mu\text{g}/\text{kg}$, respectively [3]. Comparison of the maximum levels of insecticides from the sediment samples of Kundasang from this work (Table 3) with those in river sediments throughout Sabah, indicates that vegetable farms at Kundasang are a main source of environmental contamination by endosulfan, aldrin and dieldrin. However, the maximum level of total DDT in the sediment from the Kundasang area is much lower than those found in sediments from rivers in Sabah. This is attributed to the widespread use of DDT insecticide in the malaria eradication program throughout the state prior to 1998.

For water samples from Kundasang, the organochlorine content may be compared with those reported from non-vegetable farming areas. For example, Lee et al. [8] have reported that for the Pegalan-Padas river system, the maximum levels of lindane, aldrin, heptachlor epoxide and endosulfan were from $2 - 5 \times 10^{-3} \mu\text{g}/\text{L}$ whilst dieldrin and t-DDT were 23×10^{-3} and $230 \times 10^{-3} \mu\text{g}/\text{L}$ respectively. Clearly, the maximum levels of organochlorine insecticide in the water samples from both the Cameron and Kundasang areas studied in this work were much higher than those found in non-vegetable farming areas.

For water samples from rivers in West Malaysia, the maximum levels ($\times 10^{-3} \mu\text{g}/\text{L}$) of DDT, dieldrin, heptachlor and endosulfan reported were 68.7, 0.25, 3.38 and 44.0, respectively [4]. For sediment samples, the maximum levels of heptachlor, endosulfan, and aldrin reported were 1.3, 0.96 and 0.05 $\mu\text{g}/\text{kg}$, respectively [7]. These values are very

much lower than the maximum residue levels of these insecticides in water from the Muda and Cameron Highlands areas determined in this work (Tables 2 and 3).

Conclusion

This study has shown that agricultural areas for rice paddy and vegetable cultivation are the main sources of environmental contamination by most organochlorine insecticides in Malaysia. It appears that the types of insecticide contamination are influenced by the type of agriculture. The residue levels of most organochlorine insecticides are very much higher than their levels in river water or sediments from areas that were not involved in paddy or vegetable farming reported in previous studies.

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