CHAPTER 1

INTRODUCTION

1.0 Introduction

1.1 Pesticides

Pesticides are substances used for the destruction or control of pests. They include insecticides used for killing insects, herbicides used for killing weeds and other troublesome plants, fungicides for killing fungi, rodenticides for killing rodents, such as rats and mice and molluscides for killing snails and other molluscs [1]. Pesticides are divided into various groups depending on the chemical type, such as organochlorine (OC), organophosphorus (OP) and carbamate [2].

The fate of the pesticide, once applied in the field is greatly influenced by two major factors, the biophysical features of the environmental and the physicochemical property of the pesticide itself , which may facilitate the availability and uptake of the chemical by the organism, whether that organism happens to be the target organism or otherwise. The same conditions may also cause the accelerated degradation of the pesticide or alternatively they may increase the stability of these chemicals in the fields. The more persistent pesticide will have the greater probability of being transported into the water body intact where its continued presence may lead to serious contamination of the aquatic ecosystem. Once

in the aquatic environment these chemicals are then subjected to the physicochemical properties of the water water body, and as these parameters alter so too will the fate of the pesticide with subsequent changes in their toxicity and uptake by aquatic organisms.

Within the context of the aquatic environment, physicochemical factors influencing the mobility of pesticides when applied in the field and those affecting their entry into soil water are of particular importance. In addition to a variety of environmental conditions, leaching of pesticides and subsequent contamination of local water bodies is also dependent on the physical and chemical nature of the pesticide itself, the properties of the soil and last but not least, the weather.

Lipophilicity is considered to be the most important physicochemical property of the pesticide which influences its mobility through the soil. The concentration of pesticide in soil water decreases as lipophilicity and soil adsorption increases. Hence, polar pesticides such as dimethoate and aldoxycarb are only weakly adsorbed and hence have the greatest potential for leaching while lipophilic insecticides such as permethrin and fungicides such as benomyl and triadimefon are strongly adsorbed

and present less risk of leaching [3]. In as far as the properties of the soil are concerned, the organic matter content and its accompanying correlation with physical adsorption has been determined to be an important criterion in influencing non-ionic pesticide transport, the general trend being increasing soil adsorption as the organic content increases. For pesticides which are weakly acidic in nature, on the other hand, pH of the soil plays a more important role in determining its mobility, where the maximum rate of decrease of adsorption occurs at a pH close to the pKa of the pesticide. This is due in part to the negatively charged soil surface resulting in greater hydrogen ion concentration close to the soil surface compared with the pH of the bulk. The role of the weather in influencing pesticide transport can be attributed to a number of inter-related factors, most important of which are soil temperature, water evaporation and rainfall. in general, all else being equal, when soil temperatures are low and rainfall exceeds evaporation, mobility of the pesticide increases [3].

It is also important to note at this point that when the pesticide is applied in the field it is subjected to degradation, both chemical and microbial, and the above-mentioned factors also play a role in the persistence of these chemicals. As an illustration, sulphonyl ureas which undergo acid-catalysed hydrolysis will tend

to be more persistent in alkaline soils. Similarly the weakly adsorbed pesticides has the tendency to move rapidly into subsoils where low microbial activity in addition to cooler conditions will enable them to persist [3].

While there are many factors such as salinity, hardness and turbidity which affect the fate and toxicity of pesticides in the aquatic environment, pH and temperature are two of the most influential [4]. These parameters may act directly of indirectly through their influence on the uptake of the pesticide by the organism, enzyme activity and rates of diffusion, metabolism and degradation, which in turn ultimately affect the toxicity and persistency of the pesticide with regards to the aquatic organism.

The effect of temperature on the toxicity of pesticides to aquatic fauna has been extensively studied where a direct relationship between the two parameters have been established for a great number of pesticides and variety of aquatic life forms. In general, at higher temperatures pesticides exert a greater toxic effect due to a correspondingly higher rate of metabolism and ventilation and subsequent increased uptake of the chemicals [5]. Hence the toxicity of endosulfan to trout and *Daphnia* increased with increasing temperature [6] as does the toxicity and uptake of

carbaryl to midge [7]. There are, however exceptions to this general trend as exemplified by the toxicity of permethrin to trout which is inversely related to temperature [8]. Although the uptake of pesticides increases with increase in temperature, it may also result in the increase in the rate of degradation depending upon the pesticide concerned and its degradative pathways. Different species of aquatic fauna may also react differently to changes in temperature when exposed to pesticides.

pH has also been shown to greatly affect the fate of pesticides in water [9]. Variation of influences the persistency of many pesticides in particular those which undergo hydrolysis as the major pathway of degradation in the aquatic system. Hence carbamate insecticides such as carbarly has been shown to be more persistent at low pH than under alkaline conditions [7] while the rate of hydrolysis of the S-triazine herbicides is accelerated under extreme acidic or alkaline conditions [9]. Pesticides, notably the majority of OC compounds, which do not undergo hydrolytic degradation and are not ionic, are not affected by changes in pH. On the other hand, the fate of ionic compounds are influenced by hydrogen ion concentration. This is due to the fact that the extent of dissociation of ionic compounds is dependent on the pH [10]. The toxicity of such compounds is due to the undissociated form

while the dissociated form is less toxic due to its inability to penetrate biological membranes. Examples of ionic pesticides which are subjected to changes in pH are the 2,4-dichlorophenoxyacetic acid series of herbicides, the toxic effects of which are reduced when the pH is raised due to the greater amount of the dissociated form at higher pH [10].

From the above discussion it is clear that, apart from the chemical and physical properties of the pesticide itself, pesticide transport from the point of application and the fate of the pesticide in the aquatic environment are depend upon many environmental conditions which themselves are inter-related to other parameters and biological phenomenon, in particular, pertaining to toxicity and persistency.

Although most types of pesticides will adversely affect the environment, it is the OC class of insecticides that generally poses more serious and widespread contamination risks primarily because of their toxicity, both acute and chronic, their persistent nature in the environment and their bioaccummulative characteristics. In addition to their role in the control of a broad spectrum of pests in agriculture, OC compounds have also been responsible for the control and eradication of many insect-borne

diseases affecting both human beings and livestock. Diseases such as malaria, dengue fever, typhus and dysentery, once rampant, have been either curtailed or eradicated by the use of insecticides such as DDT and lindane. In developed countries, many of these chemicals have had their use either entirely banned or severely restricted. However, they are still being used in many developing countries, in particular those located in the tropical zone. In India, for example, OC insecticides such as lindane and DDT account for more than 50% of the pesticides in use [11]. The situation is exacerbated in tropical countries as high temperatures and heavy rainfalls facilitate the dissipation of OC compounds through air and water. The risks of accidental and occupational exposure of the chemicals to man, wildlife and livestock are also greater when compared with the case in temperate countries due in part to the socioeconomic status of the people living in these areas.

1.2 Pesticides in Malaysia.

1.2.1 Pesticide usage.

The pesticide market was valued at RM301.0 million (end-user level) in 1996. Herbicides made up 75.4% (RM227.0 million) of all pesticides used in Malaysia. Insecticides accounted for 15.6% (RM47.0 million) of pesticide use while fungicides

comprised 5.3% (RM16.0 million) (Table 1.1) [12]. The value of pesticides use per hectare of crop were estimated at RM 47 in 1993 (Table 1.2) [13]. 90% of the total pesticides used in Malaysia are applied in the plantation industry, vegetable growing, rice cultivation and public health control [14]. The contribution of agriculture to the Gross National Product (GNP) was estimated at 30% in 1987, decreasing to 19% in 1990 and is expected to be at the level 13% in the year 2000 [14].

As early 1912, naturally occurring insecticides were known to be used in this country as exemplified by nicotine-chemical. After the war, their role was taken over by the OC and later on by the organophosphate and carbamates. The first few insecticides to appear in the market were DDT, lindane and the cyclodienes (aldrin , dieldrin and endrin). They were well received by farmers because there were cheap, effective, persistent, had a wide spectrum of activity and could give total kill [15].

Table 1.1: Pesticides market in Malaysia (RM million) [12]

Pesticide	1990	1991	1992	1993	1994	1995	1996
Herbicides	261.3	230.0	210.0	200.0	201.0	220.0	227.0
Insecticides	42.8	40.0	41.0	39.0	41.0	43.0	47.0
Fungicides	14.5	13.0	13.0	13.0	14.0	15.0	16.0
Rodenticides	10.5	10.0	12.0	10.0	11.0	11.0	11.0
Total	329.1	293.0	276.0	262.0	267.0	289.0	301.0

Table 1.2 : Value of the pesticides use per hectare of crop [13]

Year	Value(RM)
1988	67
1989	62
1990	61
1991	54
1992	50
1993	47

The Malaria Eradication Program (MEP) in Malaysia which was implemented in 1967 was principally based on the attempted eradication of the female anopheles mosquito , the carrier of malaria. DDT was the most widely used insecticide for these purpose in Malaysia as well as in other countries [16].

The majority of manufacturers of pesticides in Malaysia do not synthesize active ingredients but rather import them (Table 1.3) [14]. These are then formulated locally. The local production of pesticides is shown in Table 1.4 [14]. Hence, the amount of wastes generated by these industries are rather small and are generally manageable.

The pesticides Act of 1974 regulates the importation, manufacture, distribution, sale and use of pesticides in Malaysia. It is administered by the Pesticide Board of the Department of Agriculture. The Act requires for all pesticides to be registered. The data requirements are essentially in accordance with FAO guidelines. The registration is valid for three years after which they are reassessed for their continued use.

Table 1.3: Imports of pesticides in Malaysia, 1992-1993 (RM '000) [14]

Pesticides	**1992**	**1993**
Herbicides	23,479	23,290
Insecticides	48,540	52,291
Fungicides	19,832	23,463

Table 1.4: Local production of pesticides in Malaysia, 1992-1993 (RM '000) [14]

Pesticides	1992	1993
Herbicides	203,526	216,173
Insecticides	69,347	57,698
Fungicides	4,202	3,623

1.2.2 Pesticides residue in the environment

Contamination of the aquatic environment by pesticides arises mainly from their application. Contamination of surface water can occur as result of spray drift from aerial spraying and runoff from agriculture areas as a consequence of rain and to a lesser extent, leaching from the soil. Pesticide residues can also be transported in airborne particles and then deposited into the aquatic environment by rainwater. Volatilized pesticides applied in the field have also been known to be dissipated to areas far removed from the point of application. In addition to surface water, groundwater can also be contaminated by pesticide residues as a result of leaching from the soil and the inherent interaction between groundwater and contaminated surface water. The contamination of the environment by pesticides arises not only from their application but also arises from discharges accidental of intentional, of pesticides and pesticide wastes/washings from

pesticides manufacturing plants [17]. According to the United Nation Environment Programme (UNEP), less than 0.1% of the insecticides used in the third world countries actually reaches the target organisms, whereas the rest contaminates the environment [18].

1.2.3 Pesticide residues in the freshwater environment.

In Malaysia, at present there is no national or regional monitoring programme designed to investigate pesticide residues in the environment, apart from those intending to evaluate possible risk to the human population. In a study conducted by Meier and co-workers in the Krian river basin OC insecticides residues were detected in water, sediment and rice field fish [20]. Other studies conducted by different groups also have shown the presence of OCs in the environment. Table 1.5 provides an indication of the extent of contamination of OC pesticides in both biotic and abiotic components of the aquatic environment in Malaysia. In a recent study by Tan and co-workers, DDE, DDT and HCH were also found in every river surveyed in Peninsular Malaysia [19,24]. Pesticides which has been banned or whose use has been restricted, such as dieldrin, endrin and DDT continue to be detected in the environment due to their persistent character. In general, there appears to be a decreasing trend in the levels of OC

pesticide residue detected in the Malaysian environment when a comparison is made between earlier studies with more recent studies in Table 1.5. This is attributed to several factors, including the increasing use of less persistent organophosphorous and carbamate pesticides in favour of the OC class of chemical and the effectiveness of educational programmes in the safe and effective use of these chemicals conducted by the pesticide industry as well as the Department of Agriculture, directed towards end-users and suppliers of pesticides.

1.2.4 Pesticide residues in the marine environment.

Pesticides residues have also been detected in the marine environment, although the levels of contamination are expected, both in terms of variety as well as quantity to be less of threat to this environment as compared to the freshwater ecosystem. However, taking into consideration that the major agriculture areas are located in coastal plains and river valleys, many of these chemicals can persist long enough to reach the marine environment at concentrations high enough to affect marine founa and flora [25].

The level of contamination of OC pesticides in marine biota has been detected since the first surveys conducted in the mid

1970's by the Fisheries Research Institute, Malaysia (FRI). The study on OC residues in fish and shellfish in the coastal waters off the Straits of Malacca by Jothy and co-workers [26] is probably the earliest report on OC pesticide levels in marine species in Malaysia (Table 1.6). OC residues levels were found to be low in all samples analysed with the exception of levels in cockles (*Anadara granosa*) collected from Penang and Perak. Lindane levels in fish ranged from 0.001-0.012 mg/kg, dieldrin from below detection limit to 0.004 mg/kg and total DDT from 0.003-0.016 mg/kg. The total DDT concentrations in the cockles were found to be significantly higher than in the fish with a maximum value of 0.05 mg/kg. In another survey conducted in Jeram off the west coast of Peninsular Malaysia, concentrations of lindane ranged from 3-17 ng/g in various marine organisms (Table 1.6) while those of dieldrin were found to be in the range 52-232 ng/g [27].

Between 1987 and 1991 a study on OC pesticides in molluscs collected mainly from the west coast of Peninsular Malaysia was carried out by Rohani and co-workers [28] (Table 1.6). The results showed that the OC residue levels are generally low except for lindane which was found in high concentrations in some of the samples example in mussels (*Perna viridis*) in Gertak Sanggul in Penang with a level of 180.9 ng/g. Samples of oysters

(*Cronsostrea belcherei*) taken from Muar, Johor in 1990 recorded values ranging from 27.50-66.46 ng/g. Lindane level in cockles in Juru, Penang ranged from 0.22-3.01 ng/g. Alpha-endosulfan was not detected in any of the samples except for mussels from Batu Lintang, Kedah which had a value of 0.05 ng/g. None of the samples analysed contained beta-endosulfan. Aldrin was not detected in most samples, with the highest concentration of 0.24 ng/g being found in cockles from Lekir, Perak. DDT was not detected in most samples except for the oysters from Muar, Johor , with values ranging from 1.46-7.41 ng/g. Samples of cockles analysed by Rohani and co-workers from Penang and Perak had non-detectable levels for DDT except for sample in Sg. Belanak, Penang which recorded a level of 1.23 ng/g [28]. This differs markedly from the study by Jothy and co-workers, where cockles collected from Penang and Perak had DDT levels averaging 50 ng/g [26]. This difference is probably due to the phasing out of the use of DDT for the Malaria Eradication Programme.

OC pesticide levels in tiger shrimps (*Penaeus monodon*) in Ban Merbok, Kedah were reported by Liong [29]. OC pesticide residues were found to be low except for lindane (1 - 3.41 ppb). The absence of DDT was also noted and attributed to the recent cessation of the use of the chemical by Ministry of Health [29]. The

slightly higher levels of lindane could be attributed to the current usage of this pesticide in the neighbouring ricefields.

On the whole the levels of OC pesticide residues in the aquatic environment in Malaysia reflects the banned status of chemicals such as DDT, aldrin and dieldrin. As far as HCH is concerned, only the gamma isomer is allowed to be used which should give rise to a decreasing presence of the other isomers which are less insecticidal but more persistent. Previous surveys have shown the alpha and beta isomers to be present at higher concentrations than the gamma isomer as examplified by observations made by Jothy and co-workers [27]. Furthermore endosulfan residues which is also currently being used is expected to be present mainly in the freshwater ecosystem in the vicinity of the point of application due to its rather short half life.

Table 1.5: Organochlorine pesticides in biotic and abiotic components of the Malaysian aquatic environment.

Location	Survey year	Compound	Concentration (range/mean)	Ref.
Krian river basin, Perak	1981			
Water		Dieldrin	200-500ng/l	[20]
		β-HCH	100-900ng/l	
		γ-HCH	100-600ng/l	
		Aldrin	100-1800ng/l	
Sediment		Dieldrin	0.8-4.7ng/g	
		β-HCH	0.6-8.0ng/g	
		γ-HCH	0.4-0.8ng/g	
		Aldrin	0.1ng/g	
Rice field fish		Dieldrin	6.6-24.9ng/g	
		α-Chlordane	2.8-17.1ng/g	
		β-HCH	3.3-8.2ng/g	
		Aldrin	0.3-1.1ng/g	
Tanjung Karang, Selangor	1982			[21]
water		α-HCH	18-58ng/l	
		γ-HCH	10-100ng/l	
		α-endosulfan	5130ng/l	
		β-endosulfan	1700ng/l	
Penang	1984-87			[22]
Rice field+marine fish		α-HCH	2.3ng/g	
		Dieldrin	0.2ng/g	
		DDT	0.8ng/g	
		α-endosulfan	3.4ng/g	
		β-endosulfan	2.0ng/g	
Sabah(East Malaysia)	1988			[23]
Sediment		Lindane	<0.1-1.1ng/g	
		Heptachlor	<0.1-0.51ng/g	
		DDT	<0.1-34.7ng/g	
Major river systems, West Malaysia	1989-90	Dieldrin	N.D.-0.25ng/l	[19]
Water		Endrin	N.D.-3.23ng/l	
		DDT	N.D.-68.69ng/l	
		Heptachlor	N.D.-3.38ng/l	
		α-endosulfan	N.D.-44ng/l	
		β-endosulfan	N.D.-10.05ng/l	
Bernam River	1992-93	HCH	3.5ng/g	[24]
sediment		Heptachlor	1.28ng/g	
		Endosulfan	0.96ng/g	
		Aldrin	0.045ng	

Table 1.6: Organochlorine pesticide residues in marine biota from Malaysian waters.

Location	Survey year	Compound	Concentration (range/mean)	Ref.
Coastal waters off, the Strait of Malacca	1977			[26]
Cockles (*Anadara granosa*)		DDT	0.05mg/kg	
Fish		Lindane	0.001-0.012mg/kg	
		Dieldrin	<0.001-0.004mg/kg	
		DDT	0.4-0.8ng/g	
Jeram, West Coast, off Peninsular Malaysia	1985			[27]
Shrimp		γ–HCH	3ng/g	
Crap		γ–HCH	4ng/g	
Polychaete worm		γ–HCH	8ng/g	
Bivalve molluscs		γ–HCH	17ng/g	
Shrimp		Dieldrin	94ng/g	
Crap		Dieldrin	232ng/g	
Polychaete worm		Dieldrin	57ng/g	
Bivalve molluscs		Dieldrin	52ng/g	
Penang	1990			[28]
Mussels (*Perna veridis*)		Lindane	180.9ng/g	
Cockles (*Anadara granosa*)		Lindane	0.222-3.01ng/g	
		DDT	1.23ng/g	
Muar, Johor				
Oysters (*Cronsostrea belcherei*)		Lindane	27.50-66.46ng/g	
		DDT	1.46-7.41ng/g	
Batu Lintang, Kedah	1990			
Mussels		α–endosulfan	0.05ng/g	
Lekir, Perak				
Cockles		Aldrin	0.24ng/g	

1.3 Toxicity of pesticides

All chemical pesticides are potentially dangerous. There is no such thing as a completely safe chemical pesticide. Chemical pesticides are highly toxic to the pest they are intended to kill and the major repository for all chemical, including pesticides is the aquatic environment.

There is a great variation in the way different classes of pesticides affect aquatic organisms both in terms of acute and chronic toxicities just as there are variations in the toxicities of individual pesticides within each class. The toxic effects of these chemicals may also manifest themselves in many forms, e.g. physiological, morphological and behaviorial effects. Although these manifestations may not be directly nor immediately fatal , in the natural environment they may cause a decreased ability on the part of the affected organisms to maintain their physical activities in the search for food and in escaping from their enemies. The susceptibility of a particular aquatic organism to a pesticide ia also subjected to many variables notably the stage of development of the organism itself where the feeding larvae and juveniles has been determined to be the most sensitive [10].

For a number of pesticides, the mode of toxic action to aquatic flora and fauna has been determined as exemplified by the toxicity of organophosphorous insecticides which act as neurotoxins by inhibiting the neurotransmiter, cholinesterase [10,30] and that of the inhibitory effect of organochlorine insecticides upon the enzyme ATPase [10].

In general, amongst insecticides, organochlorine compounds are considered to pose the greatest threat to aquatic life forms, primarily due to the persistent character and the ability to bioaccumulate in the lipid. In addition, since OC insecticides is normarly aerially applied, the risk to aquatic organisms from field applications is accentuated. As an illustration the cyclodiene insecticide, endosulfan, which is one of the most commonly used insecticide in Malaysia is known to be extremely toxic not only to aquatic organisms such as fish but also to aquatic insects and larvae which form an important link in the ecological balance of the aquatic environment [31]. However endosulfan is relatively non-persistent compared to other OC. Various species of crustacea also demonstrate similar susceptibility to OC insecticides[10]. While cyclodiene insecticides possess high acute toxicities it is the infamous DDT and its analogs which pose the greater chronic effects, together with the added risk of bioaccumulation by aquatic

organism. This in turn, raises the real possibility of transmission of such compounds along the food chain, resulting in not only an insidious threat to environmental quality but also presenting serious implications to human health. Other insecticides such as the organophosphates, carbamates and phrethoids have moderate to high acute toxicities to aquatic organisms. The chronic toxicities of these compounds is low. The same is generally true for fungicides [10,32].

At the other end of the scale are the herbicides which have both low acute and chronic toxicities to aquatic fauna. Studies using rice field fish for example have proven that herbicides such as bensulfuron and propanil possess low acute toxicities even when applied at twice the recommended rates [33]. However, herbicides as are other pesticides, are more toxic to aquatic invertebrates that form an important source of food for many species of fish. Hence the environmental impact of these compounds seems to be indirect and certainly cannot be totally neglected, especially when taking into consideration the very high quantities that have to be initially used for effective weed control. In addition, the current tendency towards reduced tillage in agriculture in an effort to conserve soil resources has also led to an increase dependence on herbicides. Acute toxicity data of some

common pesticides to channel catfish and *pteronarcys*, a macroinvertebrate are shown in Table 1.7 [33].

Table 1.7: Common pesticides and acute toxicity levels to aquatic organisms [32]

Pesticides	**96-h $LC_{50}/\mu gL^{-1}$**	
	Channel fish	*Pteronarcys*
Endosulfan	15	2.3
Gamma BHC	105	<18
Trichlorfon	880	35
Malathion	8970	10
Carbaryl	248	-
Captafol	28	40
Paraquat	$>100 \times 10^3$	$>100 \times 10^3$
Glyphosate	130×10^3	-
DDT	16	4.1

Among the OC insecticides, DDT and HCH were widely used in Malaysia for public health, agricultural and horticultural purposes in the late 1960's and 1970's [34]. The use of these OC insecticides has been restricted in Malaysia, due to their persistent characteristics, bioaccumulative properties and toxic effect, DDT has been restricted to public health use, while as far as HCH in concerned only the γ-isomer is allowed to be used.

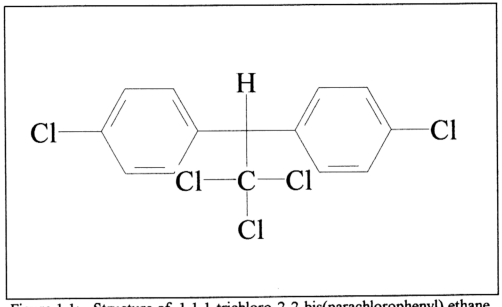

Figure 1.1: Structure of 1,1,1-trichloro-2-2-bis(parachlorophenyl) ethane (DDT)

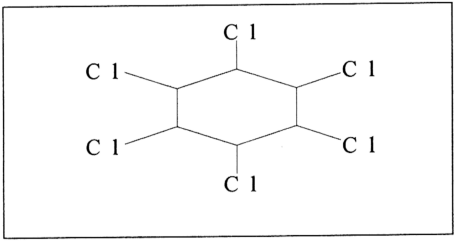

Figure 1.2: Structure of 1,2,3,4,5,6-Hexachlorocylohexane (HCH)

1.4 Model ecosystem

As a means to evaluate the distribution, fate and effects of pesticides, the model ecosystem technique has provided useful information in the assessment of pesticide impact on the ecosystem [35]. Normally this technique requires an aquarium tank which accommodates terrestrial and aquatic habitats. The degree of complexities may vary according to the number of components in the system. In addition to abiotic components, plants, microorganisms, fish and other species have been included in systems to approximate the particular ecosystem of interest.

Model ecosystem studies have been employed to elucidate the fate and distribution of pesticides in the paddy fields. The distribution and fate of radiolabeled diphenylether herbicides in rice paddy model ecosystem comprising water, sand, algae, snails, mosquitoes and fish were conducted by Lee and co-workers [36]. Over a 33-d period nitrofen and methoxy nitrofen were relatively stable and were bioconcentrated in the tissues of all the biota in the model ecosystem with the exception of water fleas. Bifonex, on the other hand, was present at relatively low levels in the tissues. Unaltered nitrofen and methoxy nitrofen were found to be the major component of the total ^{14}C extractable in fish, whereas bifonex represented only 11% of the total extractable ^{14}C in fish.

The partitioning of the insecticide carbofuran has also been examined using a model ecosystem comprising water, soil, rice seedlings and mosquito fish (Gambusia affinis) [37]. When applied at a concentration of 6ppm, which was equivalent to the recommended rate, the concentration of the insecticide in water ranged from 54ppb 3 d after application to 1ppb on the 17th day. The persistence of carbofuran in water was found to be related to the pH level, which increased from 6.8 1 d after flooding to 8.2 in 25 d.

Application methods were also found to have an important influence on the distribution of the pesticide in the paddy field ecosystem. Soil-applied ^{14}C-carbofuran partitioned into water by as much as 7% of the total applied insecticide in a model ecosystem [38]. In a similar study using a model paddy field ecosystem consisting of soil, water, rice plant and fish less than 11% of the applied labeled carbofuran was recovered from the water 24 h following incorporation into the soil surface layer, compared to a recovery of 78% in water with broadcasting as a means of application [39].

In addition to the study of pesticide distribution in agroecosystems, the model ecosystem approach has also been adapted to elucidate the fate and behaviour of chemical in the aquatic environment. The mode of uptake of ^{14}C-DDE by the aquatic organism *Chironomidae* was investigated by Derr and Zabik using a model ecosystem consisting of the organism and water. No difference were found in the amounts of ^{14}C-DDE accumulated by either live or dead *Chironomidae* as a function of exposure time. However, amount of ^{14}C-DDE concentrated by the aquatic organism was found to increase by the manipulation of water hardness. As the concentration of calcium and magnesium ion increased, a corresponding increase in ^{14}C-DDE accumulation by the organism was observed [40].

The fate of tri-, tetra-, and pentachlorobiphenyls and DDE in a laboratory model ecosystem comprising sand, water, alga, snail, mosquito and fish were conducted by Metcalf and co-workers [41]. The degradation of trichlorobiphenyl in all the organisms was observed to be more rapid than tetrachloro- and pentachlorobiphenyl. Pentachlorobiphenyl was approximately as persistent as DDE. Furthermore, a linear relationship between lipid/water partition and ecological magnification was observed [41].

The distribution and toxicity of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and 2,4,5-trichlorophenol (2,4,5-T) in an aquatic model ecosystem consisting of water, soil and catfish was conducted by Yockim and co-workers [42]. The level of 2,4,5-T and TCDD present in the water were found to be dependent on their rates of soil desorption and on their water solubilities. Radioactivity in the water from TCDD-treated tanks reached equilibrium by day 1 with concentration ranging from 2- 4μg/L while the level of ^{14}C-2,4,5-T in water, increased throughout the experiment, with a maximum of 15.2 ppb by day 30. Bioaccumulation ratios ranged between 2 - 6 x 10^3 obtained for the organisms in the TCDD-ecosystems and was less than 50 for the organism in the 2,4,5-T ecosystem [42].

The Metcalf model ecosystem consisting of water, soil, alga, snail, mosquito and fish, was used to monitor the transport of DDT from the terrestrial to the aquatic environment. DDE was found to be the major metabolite and deemed to be the ultimate environmentally-recalcitrant degradative product of DDT. DDD was also detected, ranging between 0.14 to 0.56 ppm.. Parent DDT was not detected in any of the organism or water extracts [43].

The fate and biological effects of lindane and deltametrin in a freshwater mesocosm comprising water, sediment, macrophyte and gastropod were studied by Caquet and co-workers [44]. Lindane residues persisted for as long as 19 weeks in water, 18 weeks in sediment, 14 weeks in macrophyte and 13 weeks in gastropods. Deltametrin residues persisted in water for only 96 hours. Deltametrin was detected in the macrophyte samples for 5 weeks after treatment but never in the sediment and only 24 hours after treatment in the gastropod samples [44].

The effects of the insecticide Dursban®4E (active ingredient: chlorpyrifos) on aspects of water chemistry, community metabolism and decomposition of particulate organic matter were studied in indoor freshwater microcosms [45]. Two experiments were performed; one in which all model ecosystem were dominated by macrophyte *Elodea nuttallii*, and one, using system devoid of macrophytes. In general, populations that suffered acute toxic effects of chlorpyrifos application were similar in the two types of model ecosystems, whereas secondary effects on populations of primary producers, herbivores, detritivores, and carnivores differed considerably between these systems [45].

A model ecosystem experiment consisting of water, sediment, sandworms, clams and grass shrimp was conducted to measure the accumulation of selected polychlorinated compounds [46]. All three species were found to accumulate 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF) and polychlorinated biphenyls (PCBs) from the sediment. Accumulation factors (AFs) measured for clams reached steady-state levels rapidly (10 days); however steady-state AFs values were not achieved until 70 - 120 days in the sandworms. Grass shrimp were exposed to test sediments for only 28 days at which time steady-state concentrations was not achieved for this species. The AFs for 2,4,6,8-TCDT were found to be significantly higher for shrimp than for sandworms and followed by clams [46].

In a study conducted by Leeuwangh and co-workers with four types of freshwater model ecosystems after administration of a single dose of chlorpyrifos, the population effects observed in the microecosystems, microcosms and mesocosms were found to be consistent in all experiments and with the single species tests whereas secondary effects, both for structural and functional endpoints, varied between the microecosystem and mesocosm

experiment [47]. In a six week laboratory experiment which was conducted to evaluate the effects of pesticides and microcosm size on benthic estuarine macroinvertebrate recolonization, it was found that there appears to be no major biological reason to select one microcosm size over the other for screening for contaminant effects. Hence, small trays provide savings in sample preparation and analysis [48].

In an investigation by Dauberschmidt and Dietrich in a model ecosystem consisting the mollusc *Dreissena polymorpha P.* and water, microsomes of *Dreissena polymorpha* were found to be able to biotransform the organophosphates thiometon and disulfoton significantly after 1 hour incubation at 10^0C [49]. Metabolites of thiometon and disulfoton was also detected with GCMS analysis [49].

The acute toxic response (LC_{50}) , bioconcentration factor (BCF), lethal tissue residue (LR_{50}), uptake clearance constant (K_1) elimination rate constant for tribytyltin (TBT) was examined and compared in four marine invertebrate and one marine fish species by Meador [50]. The toxic response and BCFs was vastly different among the species when exposed to the dissolved compound.

LC_{50} levels in four marine invertebrate species ranged between 3.0 - 4.7 ng mL^{-1} whereas in fish it averaged 28 ng mL^{-1} [50].

A numerical bioaccumulation model was employed by Erstfeld and Park in order to accurately predict and assess chlordane toxicant fate in natural ecosystems [51]. The model was develop based on a mass balance numerical approach and validated against data obtained from the bioaccumulation of trans and cis-chlordane into gold fish *(Carassius auratus)*. Uptake of chlordane at constant exposure was found to be 285.02 mL/g/hour whereas at non-constant exposure, a rate of 57.71 mL/g/hour was recorded. The bioconcentration factor at constant exposure was found to be 3065 while at non-constant exposure a value of recorded 3826 [51].

In a study to determine the fate of ^{14}C-DDT and ^{14}C-DDE in a model ecosystem consisting of water and soil maintained for a period of 42 d, less than 0.7% of the added labeled material were detected in soil under unflooded conditions, while under flooded condition none was detected [52]. Furthermore, the use of sterilized soil essentially eliminated ^{14}C-CO_2 release. Increased binding of p,p'-DDT and p,p'-DDE in soil were also observed under flooded unautoclaved conditions, whereas reduced p,p'-DDT

binding were observed where flooded soil was autoclaved prior to the experiment [52].

In a study conducted by Kale and co-workers using a model ecosystem consisting of water, clam and sediment for a period of 15 days, the maximum uptake of ^{14}C-DDT were found to be at the end of 3 days (746ng/g). DDE were found to be the major metabolite [53]. In an investigation with a model ecosystem consisting of water, oyster and sediment, level of ^{14}C-DDT was found to be higher in oyster compared to mussel. 94.98% of the added DDT was found in the sediment [54].

In a study conducted by Zhong and Chen with a model ecosystem consisting of water, clam and sediment, DDT was observed to rapidly accumulate in the organs of clam, mainly in the gill (32374.5 dpm/mg) followed by the digestive gland (11349 dpm/mg), mantle (10128.1 dpm/mg), foot (3676.8 dpm/mg), siphon (4870.4 dpm/mg) and adductor (999 dpm/mg). DDD amounted to 34.66% of the applied activity was found to be the major metabolite detected at the end of the study period (179d) [55]. In the similar experiment with tilapia, Zhong and Chen found that almost all the ^{14}C-DDT accumulated in various organs of tilapia within 24 h. The levels in the various organs were observed as follows : liver

(911369 dpm/mg) ,gull bladder (219467 dpm/mg) , intestine (163462 dpm/mg), brain (52852 dpm/mg), gill (43837 dpm/mg), caudal fin (26455 dpm/mg), eye (24179 dpm/mg), muscle (15890 dpm/mg) and scale (14564 dpm/mg). [^{14}C]activity in liver was found to be more than 57 times compared to muscle. DDD amounted to 6.25% of the applied activity were found to be the major metabolite followed by DDE (1.95%), DDA (1.76%) and DDMU (0.98%) [56].

In another study by Zhong and Chen with shrimp in a model ecosystem, the concentration of ^{14}C-DDT were found to be lower in the shrimp compared to tilapia. This was attributed to the crust which acted as a shield and hence reduced intake of the chemical. At the end of 24 hours highest concentration were detected in digestive gland followed by pereopod, eye, stomach, carapace, gill, intestine and muscle [57,58]. DDE (61.02% of the total applied activity) was found to be the major metabolite at the end of the study [57].

In an investigation by Matin and co-workers with a model ecosystem consisting of water, sediment, algea and mussel, ^{14}C-DDT were found to be translocated from water to sediment, algae and mussels at varying rates. Upon commencement of the

study, 94% of the applied activity was found to be present in water, while 3% and 4% were in sediment and algae respectively. 30 - 36% of the applied activity was found in algae at 3 - 6 days period. 13.28% was found in mussels on 14-day. DDT were found to be partly metabolized to DDE and DDD in algae while DDD was observed to be the only metabolite in sediments [59].

1.5 Mudflat ecosystem

Mudflats are essentially muddy land covered by the sea at high tide while being exposed at low tide. Mudflats along the western coast of Peninsular Malaysia are commonly used for the culture of marine bivalve, cockles (*Anadara granosa*). In 1994 the areas used to culture this cockles were 5041 hectares with the value estimated at RM26,788,000 (Table 1.8). The production of cockles are expected to increase 11% from the year 1990 to 2010 (Table 1.9) [60].

Some of the major agricultural areas are also located in coastal plains which are in vicinity of the cultural beds. There is every possibility that pesticide residues from agriculture land may enter the mudflats as result of spraydrift and runoff. In a recent study conducted by Rohani and co-workers the presence of OC

insecticides such DDT and lindane were detected in cockles, ranging from 0.22 - 3.01ng/g [28].

1.6 Objectives of the project.

To determine the fate and distribution of DDT and lindane in model mudflat ecosystem consisting of cockles , sediment and estuarine water.

Table 1.8: Areas used and value for aquaculture in Malaysia, 1994 [60]

Type of aquaculture	Area (hectares)	Value(RM '000)
Freshwater fish culture in ponds and disused mining pools	5754	106,902
Cockles culture in mudflats	5041	26,788
Prawn culture in brackish water ponds	1878	85,363
Marine finfish in floating net cages in coastal waters	67	60,066
Freshwater finfish in floating net cages in ponds	5	3,852
Culture of mussel and oyster on rafts/racks	17	818
Cement tank	3	1,778

Table 1.9: Projection of aquaculture production, 1990-2010('000 tonnes)[60]

Species	1990	1995	2000	2005	2010
Cockles	36.0	37.0	38.5	39.5	40.0
Mussel	1.6	5.0	10.0	15.0	25.0
Prawn	3.0	15.0	25.0	30.0	33.0
Freshwater fish (pond)	9.2	15.0	25.0	33.0	40.0
Freshwater fish (cage)	0.5	5.0	20.0	30.0	45.0
Aquarium fish	70.0	113.0	182.0	292.0	470.0

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