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5.3 Effects of Insecticides in Rice Ecosystems in Southeast Asia

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5.3.1 INTRODUCTION

Rice is an important crop worldwide, with about 144.1 million hectares being devoted to its production and about 50% of the global population being rice eaters. Of this area, more than 90% is in Asia (Medrana, 1983). Southeast Asia, which is composed of Burma, Indonesia, Cambodia, Laos, Malaysia, Philippines, Thailand, and Vietnam, produces 20% of the world's total, with a production of 77 122 000 tonnes.

The predominant production system for lowland rice is the paddy or flooded system. In the Philippines, for example, out of the total 3.5 million hectares used in production, the upland or dry system, which relies on rain, is used on only 0.4 million hectares (Mabbayad *et al.*, 1983). The rest is either irrigated lowland (65%) or rainfed lowland (35%).

Unfortunately, just like any other crop, the rice production system is also infested by a host of pests—insects, weeds, diseases, rodents, etc. They exact a heavy toll on crop production efforts. Sanchez (1983) estimates that this amounts to 8.4 million tonnes for the Philippines in 1983, while Reddy (1978) mentioned 15–30% of production potential in the Asian and Pacific region for crops in general. In an area generally regarded as having an agricultural economy in deficit, these losses become all the more significant.

To solve these pest problems, pesticides have been resorted to and it appears that their use will continue, at least in the near future, notwithstanding increased interest in integrated pest management; furthermore, integrated pest management does not preclude pesticide usage. Thus, in the Philippines, Magallona and Mercado (1978) pointed out that 30% of the area devoted to rice was treated with insecticides. Subsequently, Antazo and Magallona (1982) reported that in a government survey of five major rice-producing areas, there was 100% use of pesticides in farming. Most farmers apply pesticides twice during the cropping season while others use them three times or more. In 1984, 39% of the pesticide volume went to rice production. Staring (1984) also mentioned that in India, rice accounts for 29.5% of the value of pesticides while in Indonesia the rice farmers are the main consumers of subsidized insecticides, with about 80-90% of the total being used in this crop. Malaysia also used 28.5% of the 1980 insecticide market in rice, and Thailand reported that rice accounted for 35% of all insecticides consumed in 1980.

Given this widespread insecticide utilization in rice production and considering that pesticides are largely misunderstood, the inevitable question is, 'What are the biological effects of these compounds on components of the ecosystem?'. This is a legitimate concern which we try to address here. However, the coverage is mainly on insecticides as (1) they are the most widely used, (2) they are generally conceded to have the most dramatic environmental impact, and (3) there are more published reports on the environmental impact of this particular group among the pesticides.

5.3.2 INSECTICIDE USAGE

5.3.2.1 Evolution of Insecticide Usage

Insecticide use in rice production essentially followed the general trend for other crops, which was from organochlorines to organophosphates to carbamates to pyrethroids. Currently, the insect growth regulators (IGRs), which exert insecticidal activity through inhibition of chitin synthesis, are a very promising group of compounds. Some interest is also generated in pesticides derived from plants, especially those from all seeds of neem and related plants.

The organochlorines, with the possible exception of endosulfan and lindane, have made their exit from the overall pesticide picture. This situation, however, is not a consequence of the adverse effects on components of the paddy system, but rather because of higher biological efficacy of the newer compounds. In a sense too, the sanctions against these organochlorides meted out by developed countries were adopted by tropical developing countries without studies on their relevance to the different agroecosystem setting. However, in the case of BHC, preference is placed on the higher purity materials, preferably lindane, the 99.9% gamma-isomer, instead of the approximately 16% isomer previously available. The main reasons for this shift have been the problems, recognized in temperate countries, which are associated with the impurities.

On the other hand, technical BHC, the term used for the lower purity material, is still much cheaper than the purified materials for the paddy rice farmer and is thus more affordable. For this reason and in a display of its independence from the line of thinking that what is good for the developed countries should be automatically adopted by developing countries, India has continued to manufacture and use the technical material (Rajak, 1982). This action is also based on the finding that in the tropics, especially with flooded lowland rice

PEST/INSECTICIDE	Bangladesh	India	Indonesia	Malaysia	Philippines	Sri Lanka	Thailand
STEMBORER							
Carbofuran	-	+	+	+	+	+	+
Diazinon	+	-	+	+	+	+	-
Gamma-BHC		+	-	+	+	-	-
Endosulfan	-	-	+	+	+	+	-
GREEN LEAFHOPPER							
BPMC		-	_	+	+	-	+
Carbaryl		-	+	+	+	-	+
Carbofuran		+	+	+	+	+	+
Isoprocarb (MIPC)		-	-	+	+		+
BROWN PLANTHOPPER							
(Nilaparvata lugens)							
BPMC	-	-	+	+	+	-	+
Carbaryl	+	+	+	+	+	+	-
Carbofuran	+	+	+	-	+	-	-
Diazinon	-	+	+		+	-	-
Isoprocarb (MIPC)	-	_	+	-	+	-	+
Monocrotophos	+	-	+	-	+	-	+

Table 5.3.1 Major insecticides recommended against stemborers and hoppers in selected Asian countries*

*Compiled from Antazo and Magallona (1982); Amin et al. (1982); Malik and Khan (1982); Partoatmodjo and Alimoeso (1982); Peries (1982); Rajak (1982); Rumakon et al. (1982); URARTIP (1985).

production, lindane does not persist; see Sethunathan (1973) for an excellent review.

Organophosphates and carbamates feature prominently in the insecticide recommendations in Asian countries as seen in Table 5.3.1. The carbamates are especially useful against the hoppers, while the organophosphates' role could be traced to their being more numerous so that at least a few compounds are bound to be effective against some major insect pest. Of the carbamates, carbofuran appears to be the most widely recommended as a granule, while diazinon and monocrotophos are the organophosphates' counterparts.

The pyrethroids did not catch on in paddy rice crop protection mainly because of the resurgence problem associated with the brownplanthopper (Chelliah and Heinrichs, 1984). However, in the Philippines, cypermethrin has been registered for rice. Furthermore, Stephenson *et al.* (1984) showed that the environmental hazard from the use of this compound in rice is low. The ICRs and the botanical pesticides appear to be more promising at the moment but it remains to be seen if they will have a significant position in the future.

5.3.2.2 Rice Production and Use of Insecticides

To better understand the biological effects of insecticides, it is very important to look at when and how these compounds are applied in rice production. This pertains not only to effects on components of a rice ecosystem or organisms that by chance or design enter such an ecosystem, but also to aspects such as pollution which affect other organisms in the environment. In particular, this refers to paddy water that is intentionally drained as the rice grains start to ripen.

The growth of rice can be divided into four stages: (a) seedling stage; (b) vegetative stage; (c) reproductive stage; and (d) ripening stage. These growth stages and the insect pests usually present are shown in Figure 5.3.1. Throughout most of the growing season, water is conserved in the paddy. At the ripening stage the paddy may be drained, slightly during the milky dough stage, and then fully at the yellow ripe to full ripe stage; the latter stage is usually two weeks before harvest. This is because non-draining prolongs ripening of the grains and makes harvesting difficult.

Thus insecticide application against specific pests is carried out at the following general intervals before harvest:

seedling pests — 100 days whorl maggot — 75 days stemborers — 15-100 days hoppers — 15-100 days rice bug — 15-100 days

That insecticide application is normally directed against the major pests, e.g. the seedling pests, whorl maggots, stemborers, and hoppers, means that there

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Figure 5.3.1 Representative growth stages of the rice plant showing the associated major insect pests

is an interval of at least 20-30 days between last application and harvest, or 10-20 days from last application to drainage of pond water. This is because insecticides to control the hoppers and the borers are not necessary late in the growing period, even in the presence of the pests, short of infestation levels.

During the interval between application and drainage (or harvest), the insecticide is subject to dilution, degradation, transfer, and other factors. The small amounts that may be left at the time of draining the paddy could be transported to other bodies of water (rivers, lakes) where they could be taken up by flora and/or fauna or could settle in muds. Any effect of the pesticide depends primarily on its concentration in the substrate and the inherent susceptibility of the flora or fauna concerned.

In view of this, it is important to understand the effect of the above factors on the applied insecticide, especially under tropical conditions.

5.3.3 FATE OF PESTICIDES

5.3.3.1 The Tropical Ecosystem

On a comparative basis, the tropical ecosystem is generally conceded to result in lower pesticide persistence than the cooler temperate system. Sunlight is more



Figure 5.3.2 Mean temperatures and temperature ranges during the main rice-growing months at four locations in Asia (after Rice Production Manual, Philippines, 1969)

intense, causing not only direct photolytic effects but also such related conditions as warmer days and nights, more rapid reactions because of elevated temperature, greater volatilization and codistillation. As seen in Figure 5.3.2 for example, Los Banos, Philippines, would have a mean temperature fluctuating between about 26.5 to 28.5°C, whereas Sapporo, Japan, would have a maximum of about 21.5° and lows of about 11.5°C. Consequently, insecticide degradation in the strictly chemical sense is expected to be faster in Los Banos than in Sapporo. Support of this contention can be seen in the work of Mikami *et al.* (1980). They showed that with fenvalerate, photodegradation ranged from about 4 days in summer to 13–15 days in winter. They further calculated that at 40°N latitude, the half-life for disappearance was 4.1 and 12.4 days in summer and winter, respectively. The role of sunlight was further demonstrated by the half-life of 2, 3, and 18 days in Kudaira light clay, Azuchi sandy clay loam, and Katano sandy loam soils on exposure to sunlight, versus 55–83% remaining in these soils after 20 days without sunlight.

Rainfall is responsible primarily for the washing off of pesticides from their treatment sites, transport through erosion and solution, dilution of pesticides in aquatic environments, and for leaching and hydrolytic reactions. Rainfall is quite heavy in the Southeast Asian region, which is visited periodically by typhoons and monsoons. For selected parts of the Philippines, the pattern is



Figure 5.3.3 Rainfall pattern in some parts of the Philippines (Rice Production Manual, Philippines, 1983)

shown in Figure 5.3.3. There is a wide variation of rainfall pattern even within the tropical system, but in most cases rainfall is considered to be high. Again, rainfall is higher than in Japan or Korea so that it is expected to have a more pronounced effect on insecticides.

The warmer climate also gives rise to faster breakdown of pesticide molecules in accordance with basic chemical reaction principles. This is further reinforced by a richer, more diverse microorganism population, which may use the pesticide molecule for its metabolism or co-metabolism. Hirose *et al.* (1979; in Hashimoto, 1982) however, found that the toxicity of diazinon, fenitrothion, and phentnoate to carp and daphnids increased at higher temperature.

5.3.3.2 The Paddy Rice System

Within the tropical ecosystem, we have to consider the paddy rice system as different and unique for several reasons, among them being: (1) its essentially flooded nature; (2) dry, sun-exposed condition after flooding; and (3) distribution

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of inputs in different ways and means as a consequence of the puddled situation. As pointed out by Villegas and Feuer (1970), a puddled soil such as that of a rice paddy undergoes three major changes which can be categorized into physical, biological, and chemical.

The main physical change that occurs consists of break-up of the soil structural aggregates. This is a consequence of the flooding, which causes the soil to swell and break into small aggregates. Water loss by percolation is reduced. In view of the water layer the exchange of gases between the atmosphere and the soil is impeded. Two soil layers are therefore developed: the thin upper layer, 1-10 mm thick, which is in an oxidized state; and a reduced state lower zone; this gradient is illustrated and discussed by Sethunathan (1973). The absence of soil air brought about by the impeded gas exchange between soil and the atmosphere allows only for survival of anaerobic organisms. These organisms could be responsible for rapid pesticide breakdown, as shown for DDT (Castro and Yoshida, 1971; Guenzi and Beard, 1968; Hill and McCarty, 1967), diazinon (Sethunathan and MacRae, 1969; Sethunathan and Yoshida, 1969), and lindane (MacRae *et al.*, 1969; Sethunathan *et al.*, 1969).

With some pesticides, both the oxidative (aerobic) and reductive (anaerobic) flooded conditions could cause rapid degradation, as was found by Oyamada *et al.* (1980) for ¹⁴C-naproanilide in three different soil types.

As far as chemical change is concerned, soil pH is an important indicator. Under flooded conditions, acid soil will tend to have its pH increased while alkaline soil will have its pH lowered towards neutral. Liming, fertilizing and decomposition of organic matter are likewise expected to produce changes in the soil chemistry. Considering that the paddy soil is the ultimate sink of applied pesticides (Bajet and Magallona, 1980; Takase and Nakamura, 1974; Tejada, 1983; Varca and Magallona, 1982) these changes assume significance because it is here that pesticides could be degraded/transformed to other molecular entities. The effect of pH may be direct (hydrolysis) or indirect (mediated by specific types of microorganisms).

Another factor to consider is the occurrence of bound residues. Bound residues cannot be detected using conventional residue analysis techniques so that by effectively reducing detected residue levels, the pesticide may be considered to have a shorter persistence than is actually the case. Ogawa *et al.* (1976) found that 1/6 to 1/3 of the applied radioactivity of ¹⁴C-BPMC remained as bound residues 30 days after treatment. With isoprocarb, this amounted to 33% after 6 months (Magallona *et al.* 1985). Furthermore, our unpublished data showed 38% bound residues for carbofuran.

These bound residues could also be available to plants if they are in soil or to animals if they are in feed. Magallona *et al.* (1985) showed that rice and watermelon seedlings can take up bound isoprocarb residues, which are formed as a consequence of use in rice crop protection. Raghu and Drego (1985) likewise showed that bound lindane residues from flooded soils were bioavailable, as

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Figure 5.3.4 Changes in field paddy water pH with time of day as observed by (a) Catahan (1977); (b) Obcemea *et al.* (1977) and Bajet and Magallona (1982). (Reproduced by permission of the Philippine Association of Entomologists)

evidenced by ${}^{14}CO_2$ evolution. Formation of bound residues of lindane was favoured by neutral or alkaline conditions in a flooded soil, and was less in acidic soil.

The paddy water itself undergoes changes in pH depending on the time of day as a consequence of gas flows in the aqueous carbonate system, represented by the reaction below (Obcemea *et al.*, 1977).

$$CO_2(atm.) + H_2O \Rightarrow H_2CO_3 \Rightarrow H^+ + HCO_3^- \Rightarrow H^+ + CO_3 \Rightarrow CaCO_3$$

These pH changes are seen in Figure 5.3.4 as reported by Obcemea *et al.* (1977), Catahan (1977), and Bajet and Magallona (1982). In almost all cases, there is a pH peak ranging from 8 to 9.5 at about 1300 to 1600 hours, with lows in the morning and at dusk. Considering that the organophosphates and carbamates are easily hydrolysed at high pH, their degradation is expected to be rapid. This is documented in Figure 5.3.5 for several compounds we have studied in our laboratory. On the other hand, diazinon degradation seems to be favoured by high pH (Sethunathan and MacRae, 1969).

Some pesticides, however, appear to be persistent in the rice paddy. Thus, Takase and Nakamura (1974) as cited by Masuda (1979), observed a t1/2 of 50 days in paddy soil at 28° C for disulfoton and its five oxidative metabolites. These chemicals persisted beyond 12 weeks. On the other hand, Takase *et al.*



Figure 5.3.5 Concentration of carbofuran in paddy water after granular insecticide application (from Argente *et al.*, 1977). (Reproduced by permission of the Philippine Association of Entomologists)

(1971) recovered only 36% of the applied material in soil 10 days after application. Propaphos showed a slow decrease in paddy soil, remaining at about 10% of the initial concentration at 45 days after application (Asaka *et al.*, 1978). Masuda (1979) found that disulfoton and its oxidative metabolites were at constant levels around the rice plant for 25 days, although there was a rapid initial decline from 490 mg/kg at transplanting to 17 mg/kg after 7 days. The same trend was observed by Tanaka *et al.* (1976).

5.3.3.3 Effects on Insecticides

The net effect of the above factors is generally a rapid decline in pesticide levels in paddy rice (Sethunathan, 1973; Sethunathan *et al.*, 1975; Magallona, 1983). The loss mechanisms will not be discussed further here as they are adequately covered by Sethunathan in Section 5.2. of this book. However, for purposes of completeness in coverage, some discussions are included when we deal with the specific compounds, gamma-BHC, endosulfan, diazinon, carbofuran, isoprocarb, and BPMC.

Two additional aspects about insecticides appear to deserve mention here. They are (1) the conversion of pesticides to biologically active products, and (2) a differentiation between persistence and degradation. Some pesticides are known to be converted to biologically active products in the environment. The more familiar cases are conversion of aldrin to dieldrin by epoxidation, parathion to paraoxon by S to O substitution, heptachlor to heptachlor epoxide by epoxidation, and aldicarb to its sulphoxide and sulphone by oxidation. Carbofuran is also converted to the 3-keto and the 3-hydroxy compounds, which show some biological activity.

As far as residues in food are concerned, these biologically active transformation products are of interest, but even in this case they are considered only insofar as they are judged to be 'toxicologically significant', a term which loosely combines the magnitude of their formation and their adverse toxicological effects. Much less concern is expressed on the impact of these moieties on the environment, especially in tropical developing countries where research is not well-supported. Thus, some observed effects may not be easily reconciled with the levels or persistence of the parent compound but could well be due to these products.

Theoretically, also, a distinction should be made between 'persistence' and 'degradation'. The first term could include loss from the substrate of interest through a variety of mechanisms whereas the second term generally leads to non-toxic products. Thus we should always be concerned with the material balance in a system and this should include pesticides introduced through, say, irrigation waters. Furthermore, we have to be concerned if our ecotoxicant of interest is simply transferred from one substrate to another, and the more so if the latter is 'vulnerable'.

From the ecotoxicological standpoint, it does not necessarily follow that a degradation product innocuous against mammalian species would be harmless to other organisms as well. For example, 1-naphthol, a degradation product of carbaryl, is more toxic to goldfish (*Carassius auratus*) and killifish (*Fundulus heteroclitus*) (Shea and Berry, 1983). In fact, it is thought that 1-naphthol may be responsible for many effects attributed to carbaryl in view of this general trend with molluscs, fish, and protozoa. A BHC isomer, delta-BHC, is also virtually harmless to mammals but a very powerful molluscicide.

Of course, some compounds are transformed to other insecticidally-active compounds, as with aldrin, which is converted to dieldrin in guppy although scarcely found in *Daphnia* (Tsuge *et al.*, 1980).

5.3.4 EFFECTS OF INSECTICIDES ON SOME PADDY COMPONENTS

Biological effect is a function of the temporal concentration of the insecticide in a substrate. Immediately upon application, the concentration is still high so that chances of eliciting a response/effect from an organism are higher. As the concentration goes down, this effect may be somewhat mitigated.

The above is generally true in the case of acute effects. A more complicated phenomenon is bioaccumulation, wherein a pesticide is accumulated in the organism through continuous low-level uptake for a substrate, in most cases, water. The significance of this concentration on the organisms is generally unknown but it could cause a build-up to hazardous levels for the consumer of this organism. Some mortalities on the part of the primary organism are also possible. In most cases, once the organism is removed from contact with the pesticide, the residue level starts to decrease, indicating that the whole process is one of equilibrium between two substrates. Of course, in the case of some organisms, bioaccumulation may be viewed as a decontamination process whereby the pesticide is removed from the effective environment.

If from Figure 5.3.1, we consider that an applied pesticide is essentially confined to the paddy except for the quantity which escapes through volatilization and unintentional flooding, then its effects are likewise confined to organisms in the paddy system. These organisms include the pests themselves, the parasitoids and predators, plants, disease organisms (especially insect pathogens), and other animals. Man could be affected if he comes in and performs some tasks while pesticide levels are high or during the process of pesticide application. Fish, organisms which are not normally found in significant quantities in rice paddies, have recently become important because of the newly developed rice-fish culture. This system seeks to take advantage of water in the flooded field to raise fish in order to help fill the protein gap in most Southeast Asian countries. Furthermore, some of the fish in nearby aquatic systems may be useful for other purposes, such as predating on mosquito larvae.

Formulation type is also important in assessing ecosystem effects. Thus, the sprayables may not affect soil microorganisms to an extent comparable to the granular compounds. Conversely, non-herbivorous terrestrial organisms would not be directly affected by granulars to a significant degree but would be significantly affected by sprayables. The adverse effects of granulars may also be mitigated by the phased release, which occurs together with rapid breakdown for most compounds (Kanauchi *et al.*, 1982; Magallona, 1983; Seiber *et al.*, 1978). This may affect the availability of the compound for control so that more

economical application systems, such as root-zone application, are being tried (Siddaramappa *et al.*, 1979).

5.3.4.1 Effects of Pests

Toxicity is an expected effect of pesticides on the target pests, so it will not be discussed further here. Of interest are only (a) development of resistance, and (b) resurgence in the case of the brown planthopper, both of which may be viewed as undesirable effects on pests. In addition to the coverage here on these two topics, the papers of Nagata and Mochida (1984) on resistance development and Chelliah and Heinrichs (1984) for resurgence are recommended reading.

There have been numerous reports of insects becoming resistant to insecticides, and paddy insects are no exception. The Annual Reports of the International Rice Research Institute at Los Banos, Philippines, continually refer to development of resistance in the most important rice pests, either through comparison with greenhouse strains which have not been exposed to pesticides or to loss of effectiveness by compounds previously known to be effective. Let us summarize just a few of the studies.

- (1) In a test of a green leafhopper (GLH) collected from four sites in the Philippines vs. IRRI greenhouse cultures, low-level resistance to acephate and parathion methyl in the Palayan collections and acephate in the Sta. Maria cultures was shown (IRRI, 1981). Resistance was not detected with isoprocarb and monocrotophos.
- (2) Brown planthopper (BPH) collected at the IRRI farm, an area receiving heavy and varied insecticide treatment, was later found to be resistant to chlorpyrifos + BPMC, BPMC, and acephate (IRRI, 1983b).
- (3) Field population levels of BPH (IRRI field and farmer's field at Calauan, Laguna) had low levels of resistance to BPMC, carbaryl, carbofuran, diazinon, malathion, and MTMC when applied topically (IRRI, 1984). By contact toxicity using a Potter spray tower, six commercially available insecticides showed significantly higher BPH mortality in the greenhouse than in the field populations, indicating resistance development; there was no significant difference in the three populations for BPMC + chlorpyrifos. When these insecticides were applied as a foliar spray, there was significantly lower BPH mortality in the field than in the greenhouse population (Table 5.3.2). In the case of GLH, only with carbofuran and isoprocarb was significantly lower mortality observed in the field population.

Resurgence is the other problem associated with pesticides, notably with the BPH. It is the phenomenon whereby the use of a pesticide results in a population increase over that of untreated controls. Destruction of biological control agents has been discounted as the cause of this phenomenon (IRRI, 1981). As pointed out by Chelliah and Heinrichs (1984), this could be due to a variety of causes.

	IRRI greenhouse			IRRI field			Calauan farmer's field	
	Topical [†]	Contact [‡]	Foliar	Topical	Contact	Foliar	Topical	
BPMC	1.85	-	-	10.38 (5.61)	-	-	2.21 (1.19)	
Carbaryl	2.64	25.0	35.0	2.36 (0.89)	5.0 (5.0)	7.5	1.81 (0.69)	
Carbofuran	0.29	97.5	80.0	0.85 (2.93)	12.5 (7.8)	2.5	0.80	
Diazinon	6.34	-	-	14.21	-	-	-	
Malathion	44.58	-	-	60.78	-	-	45 (1.02)	
MIMC	3.32	-	-	2.79	-	-	46.57 (1.04)	
BPMC	-	82.5	-	-	20.0	-	2.51 (0.76)	
Monocrotophos	-	97.5	82.5	-	45.0 (2.2)	2.5 (33)	-	
BPMC + chlorpyrifos	-	65.0	60.0	-	47.5 (1.4)	7.5		
Acephate	-	52.5	75.0	-	15.0 (3.5)	7.5	-	
Isoprocarb	-	50.0	52.5	_	7.5 (6.7)	2.5 (27)	-	

Table 5.3.2 Toxicity* of some insecticides to three populations of BPH by different methods of application (mg/kg bodyweight) (after IRRI, 1984)

*Values in parenthesis are the Estimated Resistance Ratio (ERR), obtained as follows:

 $ERR = \frac{Toxicity to field population}{Toxicity to field population}$

Toxicity to IRRI greenhouse population

[†]Using purified materials

[‡]Using commercial formulations

However, some insecticides can result in resurgence, probably by providing for a favourable environment for the BPH.

At the International Rice Research Institute (IRRI, 1981) 16 insecticides used for rice control in Asia were found to cause resurgence. On the other hand, carbofuran flowable, ethylan (Perthane), technical BHC (20EC), BPMC (50EC), carbophenothion (48EC), MTMC (30EC), and chlorpyrifos (40EC) significantly reduced BPH population. Application rates seem to influence occurrence of resurgence. Thus, TN1 plants treated with decamethrin, a resurgence-inducing insecticide, had the highest level of free-amino nitrogen, but the plants sprayed with ethylan, a non-resurgence-inducing insecticide, had significantly lower levels. Insecticide application did not affect levels of starch, sugar, and total nitrogen in the plants.

5.3.4.2 Effects on Parasitoids and Predators

This aspect of pesticide use has been studied quite extensively with the BPH, a more recent major pest of rice. Among the more important of these beneficial organisms are the spiders, *Lycosa pseudoannulata* (Boes, et Str.) and *Collitrichia formosana* (Oi); the mirid bug, *Cyrtorhinus lividipennis* (Reuter), and the small water strider, *Microbelia doughlasi atrolineata*. To some extent, one may also consider the fungus, *Metarrhizium anisopliae*.

Toxicity of some insecticides to these beneficial organisms is to be expected because of their biological affinity to the target pest as well as their inevitable contact with the applied chemical. This is particularly true with chemicals that are applied by spraying. With granulars having systemic activity, these beneficial organisms should be exposed to less pesticides and because they do not feed on dead pests, toxicity to these organisms should theoretically be low.

When 12 commercially available insecticides were tested against the BPH and three of its predators, it was found that decamethrin was most toxic (IRRI, 1983a, 1984). All insecticides were toxic to *C. lividipennis*, but many were non-toxic to the spiders, *L. pseudoannulata* and *M. d. atrolineata*. This could be attributed to the greater physiological similarity of *C. lividipennis* to the BPH. On the other hand, decamethrin was selectively more toxic to the spider than the other insecticides. Carbosulfan and carbofuran were selectively toxic to the BPH compared to the first two predators. Gavarra and Raros (1973) also reported that parathion methyl is more toxic than carbaryl to *Lycosa*.

In Thailand, Rumakon *et al.* (1982) reported that one day after application of the insecticides BPMC, carbofuran, and isoprocarb, the populations of *C. lividipennis*, *Oligosita* sp., and *Tetragnatha* spp. were significantly reduced compared to controls, but these natural enemies were able to recover so that 14-15 days later their populations did not vary from controls. Amin *et al.* (1982) also reported that fenvalerate, BPMC, propuxur, endosulfan, and diazinon reduced the insect populations in a rice plot. Toxicity to *C. lividipennis* was

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Arthropod	Fenvalerate	BPMC	Propuxur	Endosulfan	Diazinon
Nilaparvata lugens	1.0(28.8) [†]	1.0(41.4)	1.0(51.9)	1.0(56.1)	1.0(46.7)
Sogatella fucifera	1.1	1.2	1.3	1.3	1.7
Cyrtorhinus					
lividipennis	1.1	0.9	1.0	1.4	1.0
Spiders Lycosa sp.,					
Tetrognatha, etc.)	1.4	3.9	2.4	3.1	1.9
Paedeaerus sp.	0.8	6.5	1.3	1.01	1.2
Casnoides sp.	0.4	0.8	0.75	3.9	1.2
Staphilinid	0.5	0.6	0.7	0.9	0.8
Carabids	1.1	0.9	1.2	0.8	0.73

Table 5.3.3 Selective toxicity* of five insecticides to some organisms in a paddy rice relative to the brown planthopper (BPH) (after Amin *et al.*, 1982)

*Based on the formula: selective toxicity =

% reduction in organisms concerned compared to controls

[†]Numbers in parenthesis refer to % reduction in BPH population.

essentially the same as that to the BPH, but the insecticides, and in particular BPMC, were less toxic to the spiders (Table 5.3.3).

Populations of the damselflies, *Agriocnemis pygmaea*, *A. femina femina*, and *Ishimura senegalensis*, which were predators of some rice pests, were reduced by insecticide treatment of paddy rice (JICA, 1981). It was suspected that in addition to killing the nymphs of damselflies which live in the soil, insecticides also affect the flying adults.

With *Anagrus* sp., a parasite of stemborer eggs, exposure to foliar spray of five insecticides resulted in more than 97% mortality. Some insecticides also reduced hatchability, while buprofezin, endosulfan, BPMC, and diazinon were not significantly different from the untreated checks (IRRI, 1981). Buprofezin was also found to be non-toxic to the three BPH predators (IRRI, 1983a, 1984).

The botanical insecticides appear to have a better selective toxicity to the predators than the conventional pesticides. Neem and Chinaberry oils were slightly toxic to the mirid bug at LD_{50} of 50 µgs/insect while Custard apple oil was moderately to highly toxic at 10–50 µg/insect. All three oils were essentially non-toxic to *L. pseudoannulata* (IRRI, 1983b).

5.3.4.3 Effects on Insect Pathogens

Some of the insecticides have also been shown to inhibit insect pathogens. For example, when mixed with culture media of *Metarrhizium anisopliae* and *Beauveria bassiana*, monocrotophos, BPMC, carbosulfan, and azinphos ethyl + BPMC reduced spore germination considerably (IRRI, 1984). However, when these insecticides were applied to the media surface, spore germination was high. Azinphos ethyl + BPMC was most toxic to *M. anisopliae*, while BPMC

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was the most toxic to *B. bassiana*. The least toxic of the insecticides to both fungi was monocrotophos.

Cadatal (1969) also found a wide variability in the effects of nine insecticides and three fungicides on the development of *B. bassiana*, and *Entomopthora* sp. Supracide, carbaryl, endosulfan, and endrin exhibited partial to complete inhibition of growth and sporulation at concentrations equivalent to the field recommendation. Fenitrothion, chlorfenvinphos, lindane, diazinon, and DDT were innocuous. The fungicides Panogen and Granosan L were toxic, while Kazumin allowed complete development.

5.3.4.4 Effects on Larger Animals

Of interest here are fishes, edible snails, toads, frogs, and ostracods. The importance of fishes as food sources as well as components of the ecosystem is well recognized so that fish toxicity data is a requirement for registration. However, the organisms used are mainly temperate fishes, and while the data thereby obtained could be a useful guide, for our purposes they cannot take the place of toxicity data obtained with tropical fishes that could be integrated with rice production. Rainbow trout or zebra fish are the recommended fishes on which to determine 96-hour LC₅₀ for registration purposes (FAO, 1981), while *Tilapia* sp. is the fish of interest to us, as it has been found suited for rice-fish culture, being edible and a fast weight gainer. As Nebeker *et al.* (1983) pointed out with endosulfan, sensitivity may vary among species over as much as three orders of magnitude. Of course, it is recognized that pesticide manufacturers in general have easier access to these two temperate fishes than *Tilapia*, and the data generated can already be good indicators of the toxicity potential of a compound.

In this regard, the data gathered by the Freshwater Aquaculture Center of the Central Luzon State University in the Philippines is of considerable importance (Table 5.3.4). In this series of tests, the Median Tolerance Limits (TL_{50} or TLM) were obtained separately using a static bioassay system. Formulated products were used in conditions simulating those in the actual paddy. This should explain some observed inconsistencies, which could be due to: (a) variations in the active ingredient content of the product; (b) differences in release rates of pesticides from granules, as in the case of diazinon; (c) differing ages of fishes; and (d) differing micro test conditions.

Azinphos ethyl is one of the most toxic materials, followed by carbofuran, BPMC + chlorpyrifos, MTMC, BPMC, isoprocarb, endosulfan, and diazinon as spray, monocrotophos, and MTMC. There is considerable inconsistency in the results with isoprocarb sold by two major suppliers and there seems to be no plausible explanation at this time. Data from our laboratory with acetone solutions of the purified carbamates show methomyl to be the most toxic followed by carbofuran, carbosulfan, and BPMC, in that order (Table 5.3.5).

	Tilapia nilotica		T. mosambica		Carassius carassius	
Insecticide	F.P.	A.I.	F.P.	A.I.	F.P.	A.I.
Methyl parathion						
(Parapest 50EC)	26.5	13.25				
BPMC						
a. Baycarb I (50%)	5.9	2.95				
II	2.8	1.4	3.15	1.58	30.5	15.25
b. Shellcarb (50%)	6.75	3.85				
Diazinon						
a. Basudin 20EC	79.5	15.9			69.5	13.9
b. Diagran 5G	77.0	3.85			45.4	2.27
Endosulfan						
(Thiodan 35EC)	8.2	2.87			7.3	2.56
Isoprocarb						
a. Mipcin (50%)	61.7	30.85			43.6	21.8
b. Hytox (50%)	6.05	3.02	6.0	3.0	34.75	17.38
MTMC (Hopcin 50EC)	1.95	0.98	3.12	1.56	29.5	14.75
Azinphos-ethyl						
(Gusathion A, 40%)	0.0275	0.011	0.23	0.009	0.086	0.03
Monocrotophos						
(Azodrin 202R, 30%)	70 (48 hrs)	21	47.6	14.28	-	-
RPMC + Chlorpyrifos	(40 1115)		(40 1115)			
(Brodan EC: 31.5%)						
(brough LC, 51.5%)	2 35	0.74	1.62	0.51		_
Carbofuran	2.55	0.74	1.02	0.51		
(Furadan F 12%)	2 27	0.27	2 24	0.27	_	_
(* ************************************	(48 hrs)	0.27	(48 hrs)			
MTMC	(10 1110)		(10 1113)			
a. Tsumacide 50WP	87	43.5	85	52.5	_	_
b. Hopcin 50EC	1.95	0.98	3.12	1.56	29.5	14.75

Table 5.3.4 24-hours TL50* of some pesticides to fishes associated with rice fish culture (consolidated from CLSU-FAC, 1978b, 1979a, 1979b, 1981b)⁺

*Expressed in ppm; formulated product (F.P.) was used in test, and data for active ingredient (A.I.) were computed based on declared active ingredient content of the product

[†]For purposes of rough comparison, the active ingredients are assumed to be equally toxic to fishes.

To reconcile pesticide use for paddy rice crop protection with the presence of fish, trenches are constructed in the middle of the paddy. One day before spray application, the paddy water is drained and the fishes are confined to the trench, which still contains some water. After several days, water is reintroduced to a depth of 7–11 cm, hopefully avoiding fish toxicity by giving adequate time for insecticide degradation. With this practice, *Bacillus thuringiensis*, BPMC, BPMC+chlorpyrifos, carbaryl, cypermethrin, isoprocarb, monocrotophos, and parathion methyl have acceptable fish recoveries, whereas azinphos ethyl is still very toxic (CLSU-FAC, 1978a, 1981a, 1981b). In persistence tests, the fish can be introduced safely by reflooding the

Insecticide	Material tested	LC 50 (mg/l)	Slope
Aldicarb	Purified	0.0013	0.31
Methomyl	Standard	0.04	0.64
Carbofuran	Purified	0.09	0.69
Carbosulfan	Standard	0.18	0.02
BPMC	Standard	0.96	0.17
Isoprocarb	Purified	1.6	0.79
Carbaryl	Purified	2.3	0.73
Landrin	Standard	5.1	0.48
MTMC	Purified	9.5	0.15

Table 5.3.5 Toxicity of some carbamate insecticides to *Tilapia nilotica* (Santiago and Magallona, 1982, reproduced with permission of the National Crop Protection Center, UPLB)

paddy within one week after application of monocrotophos, BPMC + chlorpyrifos (as spray), isoprocarb, permethrin, and carbaryl (ClSU-FAC, 1980, 1981b).

Basha *et al.* (1983) found that the order of toxicity of three insecticides to *Tilapia mossambica* was: malathion>HCH>carbaryl, with 48-hour LC50 of 0.37, 3.2, and 5.5 mg/l, respectively. They later showed that sublethal doses of these compounds cause respiratory distress in this organism (Basha *et al.*, 1984).

It should be pointed out, however, that considering the use of these fishes for food, one should be concerned not only with acute toxicity but also with bioaccumulation. Unfortunately, there is a paucity of data in this regard. However, with BPMC, carbaryl, carbofuran, chlorpyrifos, endosulfan, gamma-BHC, isoprocarb, isothioate, and XMC this does not appear to be a problem (Bajet and Magallona, 1982; Medina-Lucero, 1980; Tejada, 1983; Varca and Magallona, 1982; Gorbach *et al.*, 1971a, 1971b; Zulkifli *et al.*, 1983; Argente *et al.*, 1977; Tsuge *et al.*, 1980). On the other hand, it should be pointed out that with lindane, significant amounts accumulate in fertilized fish eggs (Ramamoorthy, 1985). Apparently, bioconcentration potential is related to water solubility and partitioning coefficient (Kanazawa, 1981).

Much less is known about the effect of pesticides on other organisms, probably because of the difficulties involved in the assay as well as in the interpretation of its importance. *Pila luzonica* Reeve, an edible freshwater snail that is considered a delicacy in some parts of the Philippines, is one organism that has been studied in some detail. Guerrero and Guerrero (1980) found gamma-BHC at 2.8 and 4.5 mg/kg in this organism and *Vivipara angularis* Muller (another edible snail), respectively, when these were cultured in rice paddies, indicating their capacity for insecticide uptake and possible bioconcentration. Low-level uptake of residue by *P. luzonica* was likewise observed with isoprocarb, BPMC, and carbofuran/carbosulfan (Bajet and Magallona, 1982; Varca and

Magallona, 1982; Tejada, 1983). This is expected for these compounds, which have high polarities, but the earlier lipophilic compounds, e.g. DDT and BHC, could have resulted in bioaccumulation by this organism. Bajet and Magallona (1982) also reported an LC50 of 25.3 mg/l for this snail.

Perez (1981) showed that rice-field ostracods are adversely affected by malathion (most toxic), carbaryl, and methyl parathion (least toxic). These ostracods are predators of the blue-green algae.

With endosulfan, Gorbach *et al.* (1971a, 1971b) observed killing of all Brachyura as well as the majority of Coleoptera and larvae of *Tipulidae* on the first day of application in a rice field in Indonesia, although these organisms reappeared after 5 days. Tubificidae, Hydrocorisidae, Cyclopidae, and Gastropoda showed no signs of mortality.

5.3.4.5 Uptake by and Effects on Plants

Of the many plant species in a paddy system, uptake of pesticides is of interest only in the rice plant and edible plants like *Ipomoea aquatica*. With rice our interest is on pesticide residues, and it has been shown that normal application of carbofuran, lindane, endosulfan, BPMC, and carbosulfan did not result in residues in grains. This is primarily due to the long interval normally observed between insecticide application and harvest, and the rapid decline of most of these pesticides in the rice paddy, despite the presence of some residues in the rice plant, e.g. as in the case of isoprothiolane which has a t 1/2 of about a month in the rice plant (Kanauchi *et al.*, 1982).

With *I. aquatica* a different picture is presented because it can be harvested and consumed as a vegetable at any time so that residues taken up by the plant could be a health hazard. Uptake of radiolabelled isoprocarb (Bajet and Magallona, 1982), BPMC (Varca and Magallona, 1982) and carbofuran (Tejada, 1983) from paddy water was shown to occur in this plant. However, it is not known what levels could be considered safe or hazardous to health, and the setting of a maximum residue limit does not appear practicable at this time.

Muralikrishna and Venkateswarlu (1984) showed that at 5-10 ppm in soil, carbaryl, endosulfan, and parathion are not harmful to the soil algal population in both flooded and unflooded soils. Carbaryl and parathion had more pronounced effects on unflooded soil, but endosulfan had little effect up to 25 ppm in both water regimes.

5.3.4.6 Model Ecosystems Studies

Some attempts have been made to evaluate the fate and effects of pesticides using model ecosystems where a food chain is constituted and the pesticide introduced. The distribution and fate of pesticides in these components are followed. This exercise presupposes that the pesticide will behave in the

ecosystem in the same manner as in the actual environment. Radiolabelled materials are often used, enabling possible quantification as well as identification of some transformation products.

One of the earlier models is that by Sastrodihardjo *et al.* (1978). Their model consisted of a series of containers wherein each paddy constituent (rice, carp, guppy, mudworms, water snails) was placed separately. Water was continuously passed through the system at the rate of 101/hour. The insecticides phosphamidon and endrin were applied at the recommended rate.

Our laboratory uses two systems, one for field level studies and another for the laboratory. These models are used primarily to assess the fate of pesticides (degradation and distribution), but some adverse effects such as fish mortality could also be observed. The laboratory model using radiolabelled compounds has the following components (Tejada, 1983):

compartment:	fully enclosed glass aquarium $40.6 \text{ cm} \text{ width} \times 74.9 \text{ cm}$
	length \times 40.1 cm depth
air circulation:	through vacuum pump with polyurethane foam trap
light:	fluorescent lamp
plant:	rice
animals:	Tilapia nilotica
	Pila luzonica

For field level studies, a concrete 289.5×23.1 cm compartment is used for growing rice; a trench can be dug in this compartment if rice-fish culture is of interest, in which case *Tilapia* fingerlings are introduced. At the appropriate time, the paddy water is drained into a pond containing fish (*Tilapia*), snails (*Pila luzonica*), toads (*Bufo marinus*), and the aquatic plant (*Ipomoea aquatica*) (Bajet and Magallona, 1982; Bautista *et al.*, 1985; Tejada, 1983; Varca and Magallona, 1982; Zulkifli *et al.*, 1983).

The emphasis in the Sastrodihardjo *et al.* (1978) model was assessment of the effect of phosphamidon. The insecticide adversely affected carps but not guppy and the water snail, *Limnaea* sp. With endrin treatment, mortality to carp, guppy, and water snail was about 20%. Neither insecticide affected the mudworms, *Tubifex* sp. Worms that were placed for 72 hours in 1 mg/l phosphamidon solution resulted in a 40% mortality in the total fish population but not in guppy. Endrin-treated worms caused greater lethal effects in guppies and rice carps.

5.3.5 FATE AND EFFECTS OF SELECTED INSECTICIDES

From Table 5.3.1 it can be seen that carbofuran, gamma-BHC, diazinon, endosulfan, and carbaryl are still widely used in rice production. The new compounds isoprocarb, BPMC, and monocrotophos have likewise gained in popularity. The discussions on persistence will be limited to only a few

compounds for which there are adequate data. It is recognized that persistence and biological effects could be mitigated by residence time of a compound in a substrate. On the other hand, a compound which may not be highly toxic may have a more significant impact if it persists in the environment for a long time.

5.3.5.1 Gamma-BHC

This compound is still useful against stemborers. Interest is in the gamma isomer, the highly purified material known as lindane. The dislike for the other isomers, especially the alpha isomer, stems from their possible carcinogenicity, longer persistence, and lack of activity against insects. Furthermore, the delta isomer is a powerful molluscicide and this could be responsible for adverse effects on edible snails.

Breakdown of this compound and three of its isomers in the flooded soil is more rapid than in unflooded soil, being mediated by anaerobic organisms such as *Clostridium* sp. (Sethunathan, 1973; Raghu and MacRae, 1966; MacRae *et al.*, 1967; Sethunathan *et al.*, 1969; MacRae *et al.*, 1969). Matsumura *et al.* (1976) also showed that gamma-BHC was metabolized by 71 of 354 microorganisms isolated from the environment.

This loss was quite rapid even at three times the recommended application rate. In the case of the gamma isomer, there was a decline from $15 \,\mu g/g$ of soil initial concentration to about $0.25 \,\mu g/g$ in 70 days, whereas in unflooded soil this remained at about $11 \,\mu g/g$. There were no significant differences in the decline of the different isomers. The degradation of BHC and other such persistent compounds as DDT, methoxychlor, and heptachlor, is aided by decomposition of organic matter, like rice stubble.

Medina-Lucero (1980) obtained essentially similar results with t 1/2 of 21.6, 5.3, 17.8, and 10.8 days in paddy soil, plants, suspended soil particles, and paddy water, respectively. Repeated application did not result in accumulation of residues. However, she observed that the alpha isomer was much more persistent, still being present after one month, whereas lindane was no longer detected. Toxic effects on fish were observed immediately after application.

In a survey of pesticides in rice paddies in Malaysia, Meier *et al.* (1983) found that in all samples of fish, sediment, and water, beta-HCH was higher than gamma-HCH. The average biomagnification ration in fish was comparable in both isomers—13.4 for the beta isomer and 11.3 for gamma-HCH.

Yamato *et al.* (1983) studied the comparative bioaccumulation and elimination of HCh isomers in the short-necked clam (*Venerupis japonica*) and guppy (*Poecilia reticulata*). Guppy rapidly bioaccumulated HCH isomers with the following bioaccumulation ratio:

alpha: 706; beta: 1043; gamma: 697; delta: 648.

Decline was constant when the organism was transferred to HCH-free water. With clams, absorption was rapid, reaching a plateau on day 3. The following bioaccumulation ratios were obtained.

alpha: 161; beta: 127; gamma: 121; delta: 272.

5.3.5.2 Endosulfan

Just like diazinon and gamma-BHC, this is an 'old' compound that is still recommended against some rice pests. It is generally applied as a spray from an emulsifiable concentrate formulation.

In the paddy system, endosulfan is not persistent and t 1/2 of 2.3 and 3.8 days were observed in suspended soil particles for endosulfan I and endosulfan II respectively (Medina-Lucero, 1980). In plants, these were 1.3 and 1.8 days respectively for the two metabolites. Being a non-persistent compound, endosulfan did not accumulate with repeated applications.

Gorbach *et al.* (1971b) also found that endosulfan residues in rice paddy fields declined rapidly both in water and in paddy mud. Immediately after treatment with 1.41 of Thiodan 35 EC per hectare, the initial concentration in the water was 0.2–0.55 mg/l. This fell to less than 0.00087 mg/l within five days. Fish mortality using *Puntius javanicus*, an endosulfan-sensitive tropical fish, was observed only on the day of application. In the case of paddy mud, the low initial level of 0.41–1.55 mg/kg was reduced by 75% after 15 days.

Massive endosulfan application in Indonesia (Gorbach *et al.*, 1971a) resulted in only 0.00046 mg/l in river and canal waters, which is about 1/3 of LC100 of 0.00125 mg/l to *P. javanicus*. A rapid decrease in residues was noted. In general, endosulfan residues were low in the preceding substrates, fish ponds, and the sea, because of degradation and dilution effects.

When endosulfan was applied to rice plants at 15, 30, 40, 60, and 90 days after transplanting and then the paddy was drained into a pond containing

shine and	Days after last spraying						
Substrate	0	5	10	20			
Paddy rice	0.08	0.08	0.002	nil			
Pond water	0.003	0.002	0.002	nil			
Paddy soil	0.50	0.19	0.09	0.13			
Rice straw	0.11	0.46	0.05	0.04			
Rice grain	0.12	0.30	0.03	0.02			
Ipomoea equatica	0.25	0.04	0.03	0.003			
Pila luzonica	0.03	nil	0.3	nil			
Pila luzonica eggs	0.01	nil	nil	nil			
Toad	nil	0.07	0.01	nil			

Table 5.3.6	Residues of endosulfan in a paddy rice system (after Bau	itista
et al., 1985)		

T. nilotica and snails, the residues were very low in snails, snail eggs, toads, and pond water (Table 5.3.6) (Bautista et al. 1985).

The toxicity of endosulfan and its metabolites to several aquatic organisms was investigated by Knauf and Schulze (1973) who obtained very variable results. In the group of the more sensitive organisms, with 48 hr LC50 of 0.001 to 0.01 mg/l, were, in order of decreasing sensitivity, the fishes *Idus melanotus*, *Lebistes reticulatus*, and *Carassius auratus*. Another group of organisms had LC50 in the 0.08 to 1 mg/l range. These were *Daphnia magna*, the insects *Aedes aegypti* and *Chironomus thummi*, and the molluscs *Planorbis corneus*, *Limnaea stagnalis*, and *Physa fontinalis*. *Tubifex tubifex* and *Artemisia solina* belonged to a third group with LC50 in the 8 to 30 ppm (mg/litre) range.

In the green alga, *Chlorella vulgaris*, the concentration of 0.001 mg/l endosulfan which was found in Indonesia by Gorbach *et al.* (1971a, 1971b) did not have any effect on cell division, photosynthetic activity, or biomass production. Photosynthetic activity remained unimpaired even with concentrations as high as 50 mg/l, but biomass and cell division were adversely affected. Measured by these parameters, a concentration of 2 mg/l would have no adverse effects.

5.3.5.3 Diazinon

This organophosphate continues to be effective against the stemborers by granular application and against the hoppers as a spray. Hydrolysis in flooded soil is aided by anaerobic organisms like *Arthrobacter*, *Flavobacterium*, and *Streptomyces*, as evidenced by: (1) faster degradation in non-sterilized than in sterilized paddy soil; and (2) isolation of these organisms which cause the hydrolysis in laboratory cultures (Sethunathan and MacRae, 1969; Sethunathan and Yoshida, 1969; Sethunathan and Pathak, 1972). Repeated application of diazinon in paddy fields enhanced the activity of these microorganisms to the extent that the efficacy of the compound against the stemborers was reduced as a consequence of rapid breakdown. In non-sterilized submerged soil, t 1/2 of 8.8 days was obtained, whereas in submerged sterilized soil it was 33.8 days.

Hirano and Yushima (1969) found that the release of granular material into paddy water reached a maximum in 3 days after application. A rapid decrease followed. Volatilization of diazinon was observed from water (Takashi and Masui, 1974); not only is this important in the control of certain pests but also in loss of residues.

5.3.5.4 Carbofuran

This is the most widely used insecticide in rice crop protection at present. It is applied as a granule because of its high inhalation toxicity. Advantage is taken of its systemic activity and relative stability in the environment (Magallona,





Figure 5.3.6 Decline curves for some insecticides in paddy water based on the work of Bajet and Magallona (1982) for isoprocarb, Zulkifli *et al.* (1983) for BPMC+ chlorpyrifos, and Tejada (1983) for carbofuran

1980). Around 1975–79 a flowable formulation was introduced but this did not catch on and health problems were also observed.

Carbofuran decline in water has been shown by Catahan (1977) to be pH dependent: at pH 7, t 1/2 is 10 days, decreasing to 0.58 days at pH 8.7, and 0.052 days at pH 10. In the field, photodecomposition contributes only a small part to the overall mechanisms. If we consider this in relation to Figure 5.3.4, which shows wide pH fluctation in paddy water, then carbofuran degradation can be expected to be rapid. This is borne out by field data. Thus, Argente *et al.* (1977) found a maximum level of 2.0 mg/l about 1 day after granular application followed by a steady decline (Figure 5.3.5). Half-life was about 4 days. In fact, Siddaramappa *et al.* (1977) reported that complete hydrolysis

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to the 7-phenol occurred in just 5 days after application because these waters have a pH range of 8.5 to 9.5. Tejada (1983) obtained similar results from carbofuran released in the rice paddy as a consequence of carbosulfan application (Figure 5.3.6).

Soil microorganisms like *Azospirillum lipoferum* and *Streptomyces* spp. have also been found to cause degradation of carbofuran (Venkateswarlu and Sethunathan, 1984). The presence of rice plants in soil also enhanced carbofuran degradation in both flooded and unflooded conditions (Brahmaprakash and Sethunathan, 1985).

High toxicity is a problem associated with this compound. Thus, application of the flowable formulation as a spray at 2 kg a.i. (active ingredient)/ha resulted in 100% *Tilapia nilotica* mortality, which persisted until residues declined to 0.03–0.6 mg/l. It was thus suggested that fish should be placed in paddies only after two weeks from broadcast application at this rate (Argente *et al.*, 1977). Broadcast application at 1 kg a.i./ha carried out four times during the rice-growing season (3, 23, 43, and 63 days after transplanting) likewise resulted in 100% fish kill (CLSU-FAC, 1979b). Root-zone application, soil incorporation, or broadcasting of granules one week before fish introduction resulted in high fish survival although Cho *et al.* (1978) reported decreases in spider populations with the use of single root-zone application of a liquid formulation and two or four broadcastings of the granule.

Carbofuran was concentrated in *Tilapia* to the extent of 68 to 189 times the concentration in water (Tejada, 1983); this is very low if compared to the 10 000 times or more reported for the earlier organochlorines. Most of the residues in fish are in the entrails, followed by the fillet, with the smallest amount in the head.

In the snail, *Pila luzonica*, the shell appears to have a protective effect so that there are slightly higher although not significantly different residues in the shell than in the flesh. A bioconcentration factor of 38.3 was obtained after 7 days.

5.3.5.5 Isoprocarb

This carbamate insecticide has become widely used against the hoppers, which are now considered the major insect pests of lowland rice. Its main market is rice so that it is registered only in a few countries, which unfortunately do not require extensive environmental impact assessment for registration.

Bajet and Magallona (1982) showed that like carbofuran, the decline of this compound in paddy water is pH dependent. At pH 8, the concentration in paddy water decreased from 5 to 0.025 mg/l after 3 hours. Half-life at pH 6 is 15 days, while at pH 7 two decline curves were observed, the first one of which lasted for about 2 days with t 1/2 of 1.4 days and the second of 88.8 days. Half-life in unflooded and flooded soils was 6.4 and 38.5 days, respectively, which is in agreement with the results of Ogawa *et al.* (1977).

Among the major metabolites in the soil, the following were tentatively identified based on the metabolic pathway proposed by Ogawa *et al.* (1977) for the compound:

(1) 2-isopropyl phenol

(2) 2-(1-hydroxy, 1-methylethyl) phenyl N-methylcarbamate

(3) 2-(1-hydroxy, 1-methylethyl) phenol

Radiolabelled isoprocarb could be detected in rice plants 6 hours after exposure, the radioactivity being concentrated on the stem and older leaves. After 2 days, this radioactivity was concentrated on the tip of the leaves. In *Ipomoea aquatica* the radioactivity was concentrated in the veins and veinlets of the old leaves, distribution being difussed in the young leaves. This uptake was demonstrated within 3 days of exposure.

In *Tilapia nilotica* and *Pila luzonica*, isoprocarb was found one day after exposure. Radioactivity was concentrated in the head area of the fish. In snails, an LC50 of 26.3 mg/l was obtained.

At the recommended rate of 0.75 kg a.i./ha isoprocarb did not decrease parasitism of *Tryporyza incertulas* (Walker) eggs (Than, 1976). However, spray application in the rice-paddy system resulted in only about 40% fish recovery (CLSU-FAC, 1978a, 1981b). *Tilapia* fingerlings may be introduced safely about 5 days after spray application (CLSU-FAC, 1980).

Quite recently, it was shown that bound residues of the compound are formed in paddy soil and this may contribute to the reported loss figures (Magallona *et al.*, 1985). These residues could be desorbed from the soil upon treatment with 0.01M CaCl₂. Low-level uptake of the bound residues has been demonstrated in rice and watermelon seedlings.

5.3.5.6 BPMC

This is another carbamate insecticide finding widespread use against the brown planthoppers and the green leafhoppers. In the Philippines, a popular emulsifiable concentrate contains 21% chlorpyrifos and 10.5% BPMC (Antazo and Magallona, 1982; URARTIP, 1985). In Indonesia, mixtures of BPMC with diazinon, fenitrothion, and phenthoate are recommended against the stemborers. (Partoatmodjo and Alimoeso, 1982).

Spray application of BPMC results in concentration of residues in rice leaves, stems, paddy water, and paddy soil, in decreasing order (NCPC, 1982; Varca and Magallona, 1982). Decline in paddy water followed pseudo first-order kinetics, with t 1/2 of 13.9 hours. In paddy soil, there was a rapid decline from 0.06 mg/kg 3 hours after spray application to 0.01 mg/kg after 3 days. In rice leaves, residues were 38.8 mg/kg 3 hours after application, but after one day only about 10% of this amount could be detected.

In a related study, Zulkifli *et al.* (1983) obtained a t 1/2 of 0.9 days in paddy water for BPMC applied using a BPMC + chlorpyrifos formulation. Residues

were taken up by *Tilapia*, with highest levels found in entrails. As a consequence of uptake, residues were found in the fillet, peaking at about 2 days after exposure to pesticide-containing water. A 5.8 times magnification factor was observed in fish versus water levels; this may be considered low.

BPMC and BPMC+chlorpyrifos are toxic to *Tilapia* (CLSU-FAC, 1978b, 1980). With the latter, fish toxicity was observed up to 15 to 20 days after application. This does not correlate very well with our findings on the t 1/2 of 0.9 days (Zulkifli *et al.*, 1983) and 13.9 hours (Varca and Magallona, 1982), but inconsistencies could be attributed to widely differing experimental conditions or possibly the formation of toxic metabolites.

5.3.6 CONCLUSION

The application of insecticides in rice production, while low on a per unit area basis in Southeast Asia compared to the more developed parts of the world, is nonetheless still a cause for concern. This is particularly so in the paddy system of rice production, where it has been averred that pesticide use has caused such organisms as the snails to be wiped out in some localities.

Limited data so far available point to some adverse effects in certain organisms within the paddy system, while with other organisms the information is not adequate to draw valid conclusions. Of course, there is a wide variability of observed effects among the organisms. One mitigating factor to consider is the rather rapid degradation of pesticides in general under flooded conditions both in the soil and water phases. These are brought about by action of anaerobic microorganisms as well as hydrolysis due to fluctuating pH, more so with the carbamates and organophosphates. Thus, with many rice pesticides currently in use and especially the carbamates, their rapid decomposition mitigates against long-term ecological effects.

The occurrence of resistance in the pests, resurgence in pest population after application of certain chemicals, and toxicity to beneficial organisms, including fishes recommended in the rice-fish culture, are among the major adverse effects discussed. In addition to these, there are other observations which cannot be considered adverse at this time, e.g. uptake by plants and limited uptake by aquatic organisms, but which nevertheless require attention.

All these problems associated with the current pesticides which, it may be pointed out, are different from the earlier group of compounds, point to the need for chemicals with more favourable environmental impact. This aspect is already being considered in the design of new chemicals but it will be a few years before these compounds become commercialized. Furthermore, research using tropical agro-ecosystems needs to be done locally. Indeed, the paucity of information shown here points to the need for greater research support if we are to understand the impact of these inputs on the tropical environment.

5.3.7 REFERENCES

- Amin, S. M., Lim, B. K., and Yong, Y. C. (1982). Pesticide (Insecticide) Use and Their Specificity on Rice in Peninsular Malaysia. Country paper presented during the Working Group Meeting on Pesticide Use Specificity, FAO, Bangkok, Thailand, Nov. 23-26.
- Antazo, T. A., and Magallona, E. D. (1982). Pesticide Use and Specificity on Rice: the Philippine Experience. Country paper presented during the FAO Working Group Meeting on Pesticide Use and Specificity, Bangkok, Thailand, Nov. 23-26.
- Argente, A. M., Seiber, J. N., and Magallona, E. D. (1977). Residues of Carbofuran in Paddy-Reared Fish (Tilapia mossambica) Resulting from Treatment of Rice Paddies With Furadan Insecticide. Paper presented at the 8th Annual Convention of the Pest Control Council of the Philippines, Bacolod City, Philippines.
- Asaka, S., Kawauchi, N., Koyoma, S., and Emura, K. (1978). *Pestic. Sci.*, **3**, 305–310 (from Masuda, T. 1979).
- Bajet, C. M., and Magallona, E. D. (1982). Chemodynamics of isoprocarb in the rice paddy environment. *Philipp. Ent.*, 5 (4), 355-371.
- Basha, S. M., Prasada Rao, K. S., Sambasna Rao, K. R. S., and Ramana Rao, K. V. (1983). Differential toxicity of malathion, BHC and carbaryl to the freshwater fish, *Tilapia mossambica* (Peters). *Bull. Environment. Contam. Toxicol.*, **31** (5), 543-546.
- Basha, S. M., Prasada Rao, K. S., Sambasna Rao, K. R. S., and Ramana Rao, K. V. (1984). Respiratory potentials of the fish (*Tilapia mossambica*) under malathion, carbaryl and lindane intoxication. *Bull. Environment. Contam. Toxicol.*, **32** (5), 570-574.
- Bautista, E. R. B., Siac, L. P., Nuguid, Z. F., Abad, L. V., de la Cruz, M. D., and Magallona E. D. (1985). *Fate of Persistent Insecticides in a Paddy Rice Ecosystem*. Report submitted to International Atomic Energy Agency for IAEA Research Contract #3400/RB.
- Brahmaprakash, G. P., and Sethunathan, N. (1985). Metabolism of carbaryl and carbosulfan in soil planted to rice. *Agric., Ecosystems and Env.*, 13, 33-42.
- Cadatal, T. D. (1969). Effect of Chemical Pesticides on the Development of Fungi Pathogenic to some Rice Insects. M.S. Thesis (unpublished), Dept. of Entomology, College of Agriculture, Univ. of the Phil., College, Laguna, Philippines.
- Castro, T. F., and Yoshida, T. (1971). Degradation of organochlorine insecticides in flooded soils in the Philippines. J. Agr. Fd. Chem., 19, 375.
- Catahan, M. P. (1977). *The Persistence of Carbofuran in the Rice Paddy Water*. M.S. Thesis in Chemistry, Univ. of the Phil. at Los Banos, College, Laguna, Philippines.
- Chelliah, S., and Heinrichs, E. A. (1984). Factors contributing to brown planthopper resurgence. *Proc. FAO/IRRI Workshop on judicious and efficient use of insecticides on rice*, pp. 107–115. International Rice Research Institute, Los Banos, Laguna, Philippines.
- Cho, S. Y., Lee, S. R., and Ryu, J. K. (1978). Effects of carbofuran root-zone placement on the spider populations in the paddy fields. *Korean J. of Plt. Prot.*, 17 (2), 99–104.
- CLSU-FAC (1978a). Technical Report No. 13. Freshwater Aquaculture Center, Central Luzon State University, Munoz, Nueva Ecija, Philippines.
- CLSU-FAC (1978b). *Technical Report No. 14*. Freshwater Aquaculture Center, Central Luzon State University, Munoz, Nueva Ecija, Philippines.
- CLSU-FAC (1979a). *Technical Report No. 15*. Freshwater Aquaculture Center, Central Luzon State University, Munoz, Nueva Ecija, Philippines.
- CLSU-FAC (1979b). *Technical Report No. 16.* Freshwater Aquaculture Center, Central Luzon State University, Munoz, Nueva Ecija, Philippines.

- CLSU-FAC (1980). *Technical Report No. 17*. Freshwater Aquaculture Center, Central Luzon State University, Munoz, Nueva Ecija, Philippines.
- CLSU-FAC (1981a). *Technical Report No. 19*. Freshwater Aquaculture Center, Central Luzon State University, Munoz, Nueva Ecija, Philippines.
- CLSU-FAC (1981b). *Technical Report No. 20.* Freshwater Aquaculture Center, Central Luzon State University, Munoz, Nueva Ecija, Philippines.
- FAO (1981). Proc. Second Expert Consultation on Environmental Criteria for Registration of Pesticides. Food and Agriculture Organization, Plant Production and Protection Paper No. 28.
- Gavarra, M. R., and Raros, R. S. (1973). Studies on the biology of the predatory wold spider, *Lycosa pseudoannulata* Boes. Et. Str. (Araneae, Lycosidae). *Philipp. Ent.*, 2 (6), 427-444.
- Gorbach, S., Haarring, R., Knauf, W., and Werner, H. J. (1971a). Residue analysis in the water system of East-Java (River Brantas, Ponds, Sea-water) after continued large-scale application of Thiodan in rice. *Bull. Env. Contam. Toxicol.*, 6 (1), 40-47.
- Gorbach, S., Haarring, R., Knauf, W., and Werner, H. J. (1971b). Residue analyses and biotests in rice fields of East Java treated with Thiodan. *Bull. Env. Contam. Toxicol.*, 6 (3), 163–199.
- Guenzi, W. D., and Beard, W. E. (1968). Anaerobic conversion of DDT to DDD and anaerobic stability in soil. *Proc. Soil Sci. Soc. Am.*, **32**, 522-534.
- Guerrero, L. A., and Guerrero, R. D. III. (1980). Preliminary studies on the culture of edible freshwater snails in Central Luzon, Philippines. CLSU Sci. J., 1 (1), 11–14.
- Hashimoto, Y. (1982). Effect of pesticides on aquatic organisms and their environment. J. Pestic. Sci., 7 (3), 281–287.
- Hill, D. W., and McCarty, P. K. (1967). Anaerobic degradation of selected chlorinated hydrocarbon pesticides. J. Wat. Pollut. Control Fed., 39, 1259-1277.
- Hirano, C., and Yushima, T. (1969). Jap. J. Appl. Ent. Ecol., 13, 174–184 (from Masuda, 1979).
- IRRI (1981). Annual Report for 1980. International Rice Research Institute, Los Banos, Laguna, Philippines.
- IRRI (1983a). Annual Report for 1981. International Rice Research Institute, Los Banos, Laguna, Philippines.
- IRRI (1983b). Annual Report for 1982. International Rice Research Institute, Los Banos, Laguna, Philippines.
- IRRI (1984). Annual Report for 1983. International Rice Research Institute, Los Banos, Laguna, Philippines.
- JICA (1981). Contributions to the Development of Integrated Rice Pest Control in Thailand. Japan International Cooperation Agency.
- Kanauchi, M., Uchida, M., and Tsuchiya, K. (1982). Persistence of isoprothiolane in paddy water and rice plants after submerged applications. J. Pestic. Sci., 7 (3), 377–383.
- Kanazawa, J. (1981). Bioconcentration potential of pesticides by aquatic organisms. Japan Pestic. Info., 39, 12–16.
- Knauf, W., and Schulze, E. F. (1973). New findings on the toxicity of endosulfan and its metabolites to aquatic organisms. *Mededelingen Fakulteit Landbouwwetenschappen*, Gent., 38, 717.
- Mabbayad, B. B., Obias, R. O., and Calendacion, R. T. (1983). Rice culture systems in the Philippines. In: *Rice Production Manual*, Philippines. College of Agriculture, University of the Philippines at Los Banos College, Laguna, Philippines.
- MacRae, I. C., Raghu, K., and Castro, T. F. (1967). Persistence and biodegradation of four common isomers of benzene hexachloride in submerged soils. J. Agr. Fd. Chem., 15, 911-914.

- MacRae, I. C., Raghu, K., and Bautista, E. M. (1969). Anaerobic degradation of the insecticide lindane by *Clostridium* sp. *Nature*, 221, 859-860.
- Magallona, E. D. (1980). *Pesticide Management*. Fertilizer and Pesticide Authority, Philippines.
- Magallona, E. D. (1983). Persistent insecticides in the tropical agroecosystem. *Philipp. Ent.*, 6 (5-6), 567-595.
- Magallona, E. D., and Mercado, B. L. (1978). Pesticide use in the Philippines. In: Pesticide Management Southeast Asia; Proc. of the Southeast Asian Workshop in Pesticide Management. BIOTROP Special Publication No. 7, pp. 71-77.
- Magallona, E. D., Bajet, C. M., and Barredo, M. J. V. (1985). Bound residues of isoprocarb in some components of the rice paddy ecosystem. In: *Quantification, Nature* and Bio-availability of Bound 1C-Pesticide Residues in Soils, Plants and Food. International Atomic Energy Agency, Vienna.
- Malik, M. A., and Khan, D. U. (1982). The process (testing, clearances, etc.) involved in recommending pesticides in Bangladesh. *Proc. FAO Working Group Meeting on Pesticide Use and Specificity*, Bangkok, Thailand, Nov. 23-26.
- Masuda, T. (1979). Behaviour of pesticides applied to rice seedlings and paddy water. In: *Sensible Use of Pesticides*, pp. 35–48. Food and Fertilizer Technology Center Book Series No. 14, Taiwan, ROC.
- Matsumura, F., Benezet, H. J., and Patil, K. C. (1976). Factors affecting microbial metabolism of v-BHC. J. Pestic. Sci., 1 (1), 3-8.
- Medina-Lucero, C. (1980). The Dynamics of Transport and Distribution of Two Organochlorine Insecticides (Lindane and Endosulfan) in a Lowland Rice Field Ecosystem. PhD Dissertation in Chemistry, University of the Philippines at Los Banos, College, Laguna, Philippines.
- Medrana, G. T. (1983). Rice Production Statistics. In: *Rice Production Manual Philippines*, pp. 1–26. College of Agriculture, University of the Philippines at Los Banos, College, Laguna, Philippines.
- Meier, P. G., Fook, D. C., and Lagler, K. F. (1983). Organochlorine pesticide residues in rice paddies in Malaysia, 1981. Bull. Environ. Contam. Toxicol., 30 (3), 351–357.
- Mikami, N., Takahashi, N., Hayashi, K., and Miyamoto, J. (1980). Photodegradation of denvalerate (Sumicidin) in water and on soil surface. J. Pestic. Sci., 5 (2), 225–236.
- Muralikrishna, P. V. G., and Venkateswarlu, K. (1984). Effect of insecticides on soil algal population. *Bull. Environ. Contam. Toxicol.*, 33 (2), 241-245.
- Nagata, T., and Mochida, O. (1984). Development of insecticide resistance and tactics for prevention. Proc. FAO/IRRI Workshop on Judicious and Efficient Use of Insecticides on Rice, pp. 93-106. International Rice Research Institute, Los Banos, Laguna, Philippines.
- NCPC (1982). Annual Report for 1981. National Crop Protection Center, College, Laguna, Philippines.
- Nebeker, A. V., McCrady, J. K., Shar, R. M., and Mcauliffe, C. K. (1983). Relative sensitivity of *Daphnia magna*, rainbow trout and fathead minnows to endosulfan. *Env. Toxicol. Chem.*, **1**, 69–72.
- Obcemea, W. N., Mikkelsen, D. S., and de Datta, S. K. (1977). Factors Affecting Ammonia Volatilization Losses from Flooded Environment Rice. Paper presented at the 8th Annual Meeting of the Crop Science Society of the Philippines, May 5-7.
- Ogawa, K., Tsuda, M., Yamauchi, F., Yamauchi, I., and Misato, T. (1976). Metabolism of 2-sec-butylphenyl N-methylcarbamate (Bassa, BPMC) in rice plants and its degradation in soils. J. Pestic. Sci., 1 (3), 219–229.
- Ogawa, K., Tsuda, M., Yamauchi, F., and Misato, I. (1977). Metabolism of 2-isopropylphenyl N-methylcarbamate (Mipcin, MIPC) in rice plants and its degradation in soils. *J. Pestic. Sci.*, **2** (1), 51.

- Oyamada, M., Igarashi, K., and Kuwatsuka, S. (1980). Degradation of the herbicide naproanilide, 1-(2-naphthoxy) propioanilide, in flooded soils under oxidative and reductive conditions. J. Pestic. Sci., 5 (4), 495-501.
- Partoatmodjo, S., and Alimoeso, S. (1982). Pesticide Use and Specificity in Indonesia. Country paper presented during the FAO Working Group meeting on pesticide use and specificity, Bangkok, Thailand, Nov. 23-26.
- Perez, G. D. D. (1981). A Bioassay of the Effects of Pesticides on Rice Field Ostracods (Crustacea) and their Consequent Predation on Blue Green Algae. B.S. Thesis (unpublished), Dept. of Life Sciences (now Institute of Biol. Sci.), University of the Philippines at Los Banos, College, Laguna.
- Peries, I. D. R. (1982). Pesticide use and specificity in Sri Lanka. Proc. FAO Working Group Meeting on Pesticide Use and Specificity, Bangkok, Thailand, Nov. 23-26.
- Raghu, K., and MacRae, I. C. (1966). Biodegradation of the gamma isomer of benzene hexachloride in submerged soils. Science, 154, 263-264.
- Raghu, K., and Drego, J. (1985). Bound Residues of Lindane: Magnitude, Microbial Release, Plant Uptake and Effects on Microbial Activities. Paper presented at the 3rd Research Coordination Meeting on Isotopic Tracer-aided Studies on Bound Residues in Soils, Plants and Food, Gainesville, Florida, USA, March 25-29.
- Rajak, R. L. (1982). India. Country paper presented during the FAO Working Group Meeting on pesticide use and specificity, Bangkok, Thailand, Nov. 23-26.
- Ramamoorthy, S. (1985). Competition of fate processes in the bioconcentration of lindane. Bull. Environment. Contam. Toxicol., 34 (3), 349-358.
- Reddy, D. B. (1978). Future trends of pesticide use in the world with particular reference to Asia and the Pacific. In: *Pesticide Management Southeast Asia; Proc. Southeast Workshop on Pesticide Management*. BIOTROP Special Publication No. 7, pp. 1–23.
- Rice Production Manual (1969). College of Agriculture, University of the Philippines, Philippines.
- Rice Production Manual (1983). University of the Philippines at Los Banos, College of Agriculture, College, Laguna, Philippines.
- Rumakon, M., Vungsilabutr, P., and Katanyakul, W. (1982). *Thailand*. A country paper presented during the FAO Working Group Meeting on pesticide use and specificity, Bangkok, Thailand, Nov. 23–26.
- Sanchez, F. F. (1983). Pest Management: status and potential contribution to Philippine agriculture. *Philipp. Ent.*, 6 (5-6), 595-606.
- Santiago, D., and Magallona, E. D. (1982). Toxicity of different insecticides to *Tilapia* nilotica. 1981 Annual Report. National Crop Protection Center, College, Laguna, Philippines.
- Sastrodihardjo, S., Adianto, M., and Yusoh, M. D. (1978). The impact of several insecticides on soil and water communities. Proc. Southeast Asian Workshop on Pesticide Management, pp. 117-125. Bangkok, Thailand.
- Seiber, J. N., Heinrichs, E. A., Aquino, G. B., Valencia, S. L., Andrade, P., and Argente, A. M. (1978). Residues of carbofuran applied as a systemic insecticide in irrigated wetland rice: implications in insect control. *IRRI Research Paper 17* (May).
- Sethunathan, N. (1973). Microbial degradation of insecticides in flooded soil and in anaerobic cultures. *Residue Reviews*, 47, 143-165.
- Sethunathan, N., and MacRae, I. C. (1969). Persistence and biodegradation of diazinon in submerged soils. J. Agr. Fd. Chem., 17 (2), 221-225.
- Sethunathan, N., and Yoshida, T. (1969). Fate of diazinon in submerged soil. Accumulation of hydrolysis product. J. Agr. Fd. Chem., 17, 1192–1195.
- Sethunathan, N., and Pathak, M. D. (1972). Increased biological hydrolysis of diazinon after repeated application to rice paddies. J. Agr. Fd. Chem., 20, 586-589.

- Sethunathan, N., Bautista, E. M., and Yoshida, T. (1969). Degradation of benzenehexachloride by a soil bacterium. *Can. J. Microbiol.*, **15**, 1349-1354.
- Sethunathan, N., Siddaramappa, R., Gowda, T. K., and Rajarah, K.P. (1975). Pesticide residue problems in flooded rice ecosystem. Proc. FAO/UNEP Expert Consultation on Impact Monitoring of Residues from the Use of Agricultural Pesticides in Developing Countries. Rome, Sept. 29-Oct. 3.
- Shea, T. B., and Berry, E. S. (1983). Toxicity of carbaryl and 1-naphthhol to goldfish (*Carassius auratus*) and killifish (*Fundulus heteroclitus*). Bull. Environment. Contam. Toxicol., 31 (5), 526-529.
- Siddaramappa, R., Tirol, A. C., Seiber, J. N., Heinrichs, E. A., and Watanabe, I. (1977). Loss of insecticide carbofuran (Furadan) from standing water and in flooded soil. Paper presented at the 8th Annual Convention of the Pest Control Council of the Philippines, Bacolod City, Philippines.
- Siddaramappa, R., Tirol, A., and Watanabe, I. (1979). Persistence in soil and absorption and movement of carbofuran in rice plants. J. Pestic. Sci., 4 (4), 473-479.
- Staring, W. D. E. (1984). Pesticides: Data Collection Systems and Supply, Distribution and Use in Selected Countries of the Asia-Pacific Region. Economic and Social Commission for Asia and the Pacific, Bangkok, Thailand.
- Stephenson, R. R., Choi, S. Y., and Olmos-Jerez, A. (1984). Determining the toxicity and hazard to fish of a rice insecticide. Crop Prot., 3 (2), 151-165.
- Takase, I., and Nakamura, H. (1974). Nippon Nogeikagaku Kaishi, 48, 27-32 (from Masuda, T. 1979).
- Takase, I., Tsuda, H., and Yoshimoto, Y. (1971). Jap. J. Appl. Ent. Zool., 15, 63-69 (from Masuda, T. 1979).
- Takashi, I., and Masui, A. (1974). Jap. J. Appl. Ent. Zool., 18, 171-176 (from Masuda, 1979).
- Tanaka, F., Usuda, Y., Shibata, Y., Yakumaru, K., Yamamoto, M., Kondo, T., Hayashi, K., and Aida, S., (1976). Zenno Hoyakushiken Seiseki, 501–509 (from Masuda, T. 1979).
- Tejada, A. W. (1983). Fate of carbosulfan in rice paddy-ecosystem. PhD Dissertation, University of the Philippines at Los Banos, College, Laguna, Philippines.
- Than, H. (1976). *Ecology of the Yellow Rice Borer*, Tryporyza incertulas (*Walker*) and *its Damage to the Rice Plant*. M.S. Thesis (unpublished), Dept. of Entomology, College of Agriculture, University of the Philippines, College, Laguna, Philippines.
- Tsuge, S., Nishimura, T., Kazano, H., and Tomizawa, C. (1980). Uptake of pesticides from aquarium tank water by aquatic organisms. J. Pestic. Sci., 5 (4), 585-593.
- URARTIP (Unified Rice Action Research and Training Intensification Programme). (1985). 16 Steps Masagana-99 Rice Culture. Bureau of Agricultural Extension. Diliman, Quezon City.
- Varca, L. M., and Magallona, E. D. (1982). Residues of BPMC (2-sec-butyl phenyl Nmethylcarbamate) on some components of a paddy rice ecosystem. Proc. 13th Annual Convention of the Pest Control Council of the Philippines, Baguio City, May 5–8.
- Venkateswarlu, K., and Sethunathan, N. (1984). Degradation of carbofuran by Azospirillum lipoferum and Streptomyces spp. isolated from flooded alluvial soil. Bull. Environment. Contam. Toxicol., 33, 556–560.
- Villegas, L. M., and Feuer, R. (1970). The 'lowland' or flooded soils. In: *Rice Production Manual*, pp. 68–73. UPLB/IRRI.
- Yamato, Y., Kiyonaga, M., and Watanebe, T. (1983). Comparative bioaccumulation and elimination of HCH isomers in shortnecked clam (*Venerupis japonica*) and guppy (*Poecilia reticulata*). Bull. Environ. Contam. Toxicol., 31 (3), 352–359.
- Zulkifli, M., Tejada, A. W., and Magallona, E. D. (1983). The fate of BPMC and chlorpyrifos in some components of a paddy rice ecosystem. *Philipp. Ent.*, 6 (5-6), 555-565.