

5.2 *Biodegradation of Pesticides in Tropical Rice Ecosystems*

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5.2.1 INTRODUCTION

Tropical and/or subtropical conditions exist in most of the developing countries. Hot and humid environments in the tropics and subtropics favour the build-up of a myriad of pathogens and insects harmful to the agricultural and plantation crops of economic importance. Yet, use of pesticides in the developing countries of the tropics has been negligible. For instance, pesticide use in India amounted to only 338 g/ha as compared to 1490 g/ha in Japan (Krishna Murti and Dikshith, 1982). This does not necessarily imply that problems of pesticide contamination do not exist in developing countries. In recent years, with the advent of modern agricultural technology in developing countries, there has been a steady increase in the use of pesticides on some economically important crops. There is concern over environmental problems arising from the massive use of pesticides in irrigated rice and other crops (cotton in particular), even in developing countries of the tropics.

In India and probably many other countries in the tropics, insecticides outstrip other groups of pesticides in consumption, while herbicides top the list in developed countries (Table 5.2.1). In recent years, the use of organochlorine pesticides has been steadily declining in developed countries due to concern over their long-term persistence and consequent ecological disturbances in the environment. But, organochlorine insecticides account for 70% of all pesticides used in India during 1983–84 (Anonymous, 1984) and probably in many developing countries, because of their low price, indigenous availability, broad-spectrum action, and long-term efficacy.

Recently, however, there has been concern in several developing countries over the environmental hazard from the heavy and regular use of organochlorine pesticides in public health and agriculture. This concern, based on the persistence data generated from studies in temperate environments of the developed countries, is unwarranted at least for some organochlorines, such as hexachlorocyclohexane (HCH). According to reports, hot and humid conditions

Table 5.2.1 Consumption of pesticides per category in India and developed countries.
From Mrinalini (1983). Reproduced with permission from Pesticides, Bombay

Pesticide group	India	Developed countries
Insecticides	75%	35%
Herbicides	7%	45%
Fungicides	15%	15%
Others	3%	5%

such as exist in most of the developing countries of the tropics and subtropics effect more rapid breakdown of certain biodegradable pesticides than cooler conditions in temperate environments (Talekar *et al.*, 1977; 1983a, 1983b). Thus accumulation problems from the intensive use of pesticides may be less pronounced under tropical conditions than under temperate conditions. Again, persistence of pesticides in the environment is greatly influenced by the cultivation practices used for specific crops. For instance, the common practice of flooding in rice culture and of organic amendments for most agricultural crops hastens the degradation of several pesticides. The recent trend to ban or restrict the use of certain organochlorine pesticides in some developing countries based on research conducted elsewhere, mostly under temperate conditions not relevant to local tropical situations, merits caution. Admittedly, information on the fate and behaviour of pesticides under tropical conditions is fragmentary. Available literature (Sethunathan, 1973; Sethunathan *et al.*, 1977; Sethunathan and Siddaramappa, 1978; Sethunathan *et al.*, 1982, 1983; Rajagopal *et al.*, 1984a) indicates that biodegradation is an important means of detoxification of several commonly used pesticides, insecticides in particular, in tropical soils. In this section, an attempt is made to review the progress made in research on the degradation of certain pesticides in tropical soils and, wherever possible, to compare their relative persistence in tropical and temperate soils.

5.2.2 ORGANOCHLORINES

Among the organochlorines, hexachlorocyclohexane (HCH) is probably the most widely used insecticide in many developing countries. Hexachlorocyclohexane accounts for about 56% of all pesticides used in India. Organochlorine pesticides, HCH, DDT, methoxychlor, heptachlor, aldrin, dieldrin, and endrin, were considered as recalcitrant to biodegradation, because of their extreme stability and consequent long-term persistence (for several years) in aerobic soil and water environments. But, not all these insecticides are stable in anaerobic environments. The first convincing evidence of anaerobic instability of an organochlorine was provided when HCH disappeared fairly rapidly (within 90 days) from a tropical Philippine soil upon flooding, a common practice in rice culture (Raghu and MacRae, 1966).

Interestingly, gamma-HCH was not accumulated in the soil even after repeated application of HCH granules to flooded rice paddies in the Philippines (IRRI, 1967). Flooded rice fields were treated with HCH granules at the rate of 3 kg/ha, with two or four applications per season for two seasons in a year and for two years. Irrespective of the total amount of gamma-HCH applied in two years (a total of 48 kg/ha at four applications/season and 24 kg/ha at two applications/season), its concentration declined to low levels in soil (0.014–0.018 ppm) and water (0.1 ppm), and was identical in both plots within 20 days after every application.

Most recently, Yoshida and Yamaya (1984) studied the relative persistence of gamma-HCH in 11 soil samples collected from temperate, subtropical, and tropical regions under submerged conditions. Most of the gamma-HCH was degraded in eight soil samples from all regions in 70 days, and the rate of degradation increased with increased incubation temperature in the range of 20°C to 40°C. Interestingly, a tropical soil (Seputih soil from Indonesia) effected most rapid degradation of gamma-HCH, especially at higher temperatures.

That the alpha, beta, and delta isomers of HCH, like gamma-HCH, show a greater persistence in temperate soil (Tsukano, 1973) than in tropical soil (Castro and Yoshida (1974) under flooded conditions is best illustrated by data derived from two independent studies and brought together in Figure 5.2.1. In tropical soil (Philippines), all the four isomers of HCH reached low levels (3.4–17.1% of the original level) in 21 days. But, in temperate soil (Japan), only gamma-HCH declined to low levels (about 7% of the original level), while other isomers persisted with recoveries of 50–75% of the original level even after 28 days. As for the HCH isomers, other organochlorines, such as DDT, methoxychlor, heptachlor, and endrin, but not aldrin and dieldrin, were more rapidly decomposed in flooded soils than in non-flooded soils (Yoshida and Castro, 1970; Castro and Yoshida, 1974). Degradation occurred only in non-sterile soil samples (Castro and Yoshida, 1971).

A flooded soil differs from a non-flooded soil in physical, chemical, and microbial characteristics (Ponnamperuma, 1972; Gambrell and Patrick, 1978). Within a few days after flooding a soil becomes predominantly anaerobic due to diminished oxygen supply. Following flooding, the pH of acid or alkaline soils stabilizes at near neutrality while the redox potential drops rapidly. Soil constituents (nitrate, ferric, manganese, sulphate ions) are almost sequentially reduced under submergence.

More importantly, under such reducing conditions the anaerobes (facultative and obligate) become dominant. It is these anaerobic microorganisms that effected the rapid degradation of HCH/DDT and other anaerobically unstable organochlorines. Specifically, in flooded soils an obligate anaerobe, *Clostridium sphaenodes*, isolated from HCH-enriched flooded soil was capable of degrading alpha- and gamma-HCH, but not beta- and delta-HCH, under anaerobic conditions (MacRae *et al.*, 1969; Sethunathan *et al.*, 1969; Heritage and MacRae,

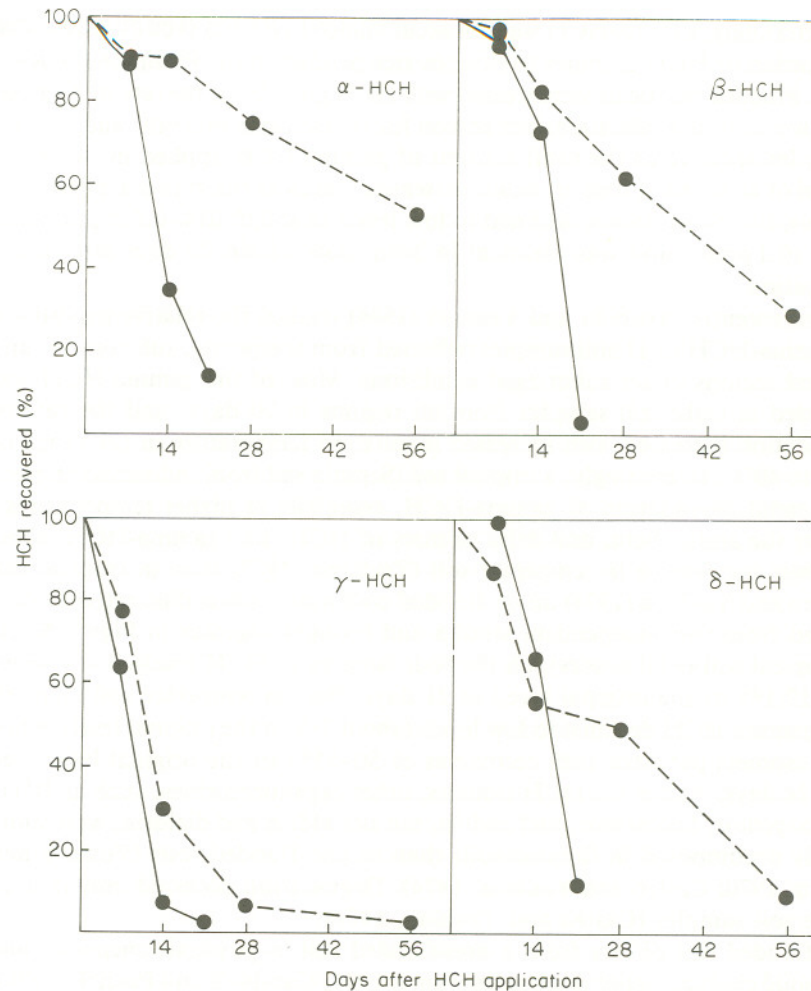


Figure 5.2.1 Relative persistence of isomers of hexachlorocyclohexane (HCH) in tropical (●—●) and temperate (●—●) soils under flooded conditions. Adapted from Castro and Yoshida (1974) (tropical soil) and from Tsukano (1973) (temperate soil)

1979). The same bacterium also degraded related organochlorines, such as DDT, methoxychlor, and heptachlor (Sethunathan and Yoshida, 1973a) under anaerobic conditions. In a more recent study (Yoshida and Yamaya, 1984) with soil samples from temperate, subtropical, and tropical regions, a gamma-HCH degrading bacterium isolated from each of eight soils was identified as *Clostridium* sp. Moreover, the gamma-HCH degrading activity of the isolates was more pronounced at 40°C than at 20°C and 30°C. Under actual field conditions in the tropics, high soil temperatures may accelerate the degradation

of HCH isomers, especially under flooded soil conditions. Indeed, a rise in soil temperature from 20°C to 40°C accelerated the reduction of the soil under submergence (Cho and Ponnamperna, 1971), and such intense reducing conditions would catalyze the degradation of HCH isomers (Siddaramappa and Sethunathan, 1975), mediated essentially by the dominant anaerobic microorganisms.

Evidence suggests that the microorganisms effect the degradation of HCH by a process known as co-metabolism, i.e. without utilizing it as an energy source for proliferation. In such co-metabolic reactions, an adequate supply of organic sources would accelerate the proliferation of these anaerobic microorganisms and thereby the degradation of pesticides in soil environments. In fact, the addition of organic sources, such as rice straw or green manure, stimulated the degradation of HCH and DDT in a soil under flooded, but not under non-flooded conditions (Guenzi and Beard, 1968; Yoshida and Castro, 1970; Siddaramappa and Sethunathan, 1975; Ferreira and Raghu, 1981).

Worldwide research has shown the ubiquitous occurrence, in anaerobic ecosystems, of a wide range of microorganisms, bacteria in particular, that readily degrade DDT (Sethunathan *et al.*, 1983). Thus, available evidence indicates that gamma-HCH and DDT undergo fairly rapid degradation in microbially active soils capable of attaining redox potential of -50 to -100 mV upon flooding (Sethunathan and Siddaramappa, 1978).

A flooded soil planted to rice differs from a flooded unplanted soil in physico-chemical and microbiological characteristics. A flooded planted soil is more dynamic than a flooded unplanted soil, because of the intense microbial activity and complex reactions in the nutrient-rich rhizosphere of the rice plant. Besides, a flooded unplanted soil is predominantly anaerobic, while significant transport of oxygen from the foliage of the rice plant to the rhizosphere occurs in a flooded soil planted to rice. However, in a study on the stability of HCH isomers in a flooded soil with and without rice plants, alpha- and gamma-HCH decreased to less than 5% of the original level in 30 days in both planted and unplanted soils (Table 5.2.2; Brahma Prakash *et al.*, 1985). Beta-HCH appeared to be more stable than alpha- and gamma-HCH, with a recovery of 30.9% from the planted soil and 50.6% from unplanted soil. Measurements of redox potential showed that flooded soil planted with rice registered a potential of $+200$ mV as compared to a potential of -300 mV in flooded unplanted soil. Evidently, degradation of aerobically stable isomers of HCH in a flooded soil was not retarded in the presence of rice plants despite the ability to transport oxygen to the root region and to maintain the flooded soil in an aerobic state. Possibly, degradation of HCH isomers occurred at anaerobic microsites, which abound in a flooded soil planted with rice.

The use of biodegradable organochlorine insecticides in flooded rice paddies, despite their instability in anaerobic environments, still poses problems of great concern:

Table 5.2.2 Mineralization of different isomers of HCH in a flooded soil with and without rice plants (Brahmaprakash *et al.*, 1985). Reproduced with permission from Springer-Verlag & Heidelberg

Days/ Fraction	Alpha-HCH*		Beta-HCH*		Gamma-HCH*	
	Unplanted	Planted	Unplanted	Planted	Unplanted	Planted
	(percent radioactivity recovered)					
O day						
HCH	87.9	78.7	80.6	76.3	96.8	82.3
Soil-bound	0.5	0.8	0.5	0.6	0.4	0.5
15 days						
HCH	18.9	22.1	50.7	44.3	5.2	8.22
Soil-bound	1.1	1.2	1.4	1.3	1.1	0.95
30 days						
HCH	5.5	4.3	50.6	30.9	2.2	2.4
Soil-bound	1.9	1.5	2.1	2.3	1.5	1.3

*¹⁴C-alpha-HCH, ¹⁴C-beta-HCH, and ¹⁴C-gamma-HCH were added at 1.66×10^5 dpm/100 g of soil

- (i) Commercial formulations of HCH contain several isomers, of which the gamma isomer is readily biodegradable. Beta-HCH, albeit a minor constituent in HCH formulations, is more resistant to anaerobic degradations than gamma-HCH and, therefore, accumulates in the environment, raising concern over its entry into the food chain. Although beta-HCH undergoes degradation, but at a slow rate, in flooded soil, attempts to isolate a microorganism capable of degrading beta-HCH in pure culture have been unsuccessful.
- (ii) Gamma-HCH, despite its instability in anaerobic flooded rice field soils, accumulates in rice straw, a major cattle feed in several countries, and eventually enters the food chain.
- (iii) DDT is readily degraded in anaerobic environments, but its degradation product, DDD, which is as toxic as DDT, resists further degradation. Likewise, endrin is unstable in anaerobic systems (Gowda and Sethunathan, 1976, 1977) but its degradation products are highly stable. Thus, there is a need to understand the toxicological significance of such stable metabolites formed from parent pesticides.

5.2.3 ORGANOPHOSPHATES

Parathion, until recently the most widely used organophosphorus insecticide in agriculture and public health, has now been banned from commercial use because of its high mammalian toxicity. However, parathion still serves as a model insecticide in research on the metabolism of organophosphorus pesticides in soil and water environments. Degradation of parathion in a tropical

(Philippines) rice soil occurred more rapidly under flooded conditions than under non-flooded conditions (Sethunathan and Yoshida, 1973b; Sudhakar Barik *et al.*, 1979) and temperate (Katan *et al.*, 1976) soils proceeded essentially by nitro group reduction to aminoparathion after the first application. The rate of degradation of parathion in both soil samples was accelerated after two or three applications of parathion or its hydrolysis product *p*-nitrophenol (Sudhakar Barik *et al.*, 1979; Ferris and Lichtenstein, 1980). Pretreatment of the temperate soil (cranberry) with parathion or *p*-nitrophenol led to the accelerated mineralization of subsequently added parathion to CO₂ (Ferris and Lichtenstein, 1980).

In studies with tropical soil, CO₂ was not quantified, but the pathway of parathion degradation shifted from nitro group reduction after the first application of parathion, essentially to hydrolysis after two or three applications of parathion or *p*-nitrophenol (Sudhakar Barik *et al.* 1979). The shift in the pathway of degradation was a direct consequence of the proliferation of parathion-hydrolysing microorganisms that utilized *p*-nitrophenol as the energy source.

A *Pseudomonas* sp. ATCC 29353, isolated from a flooded tropical soil after three repeated additions of parathion, readily hydrolysed parathion and then metabolized *p*-nitrophenol to nitrite (Siddaramappa *et al.*, 1973) and CO₂ (Sudhakar Barik *et al.*, 1976). Such accelerated biological hydrolysis of parathion has been demonstrated also in a temperate soil after repeated applications of the insecticide (Munnecke *et al.*, 1982). According to these observations, accelerated degradation of parathion through biological hydrolysis can be of common occurrence in both tropical and temperate regions. Parathion is short-lived in soil environments, especially under flooded conditions. This necessitates the frequent application of this insecticide at short intervals for efficient control of harmful pests. But, such frequent applications of parathion may, in turn, promote the build-up of parathion-hydrolysing microorganisms that undermine its efficacy.

Methyl parathion and fenitrothion, structurally related to parathion, are used increasingly in agriculture because of their relatively low mammalian toxicity. Adhya *et al.* (1981a) reported fairly rapid decomposition of parathion, methyl parathion, and fenitrothion to their respective amino analogues in a tropical (Indian) soil under flooded conditions. There are some independent reports on the degradation of fenitrothion in tropical (Indian) and temperate (Japanese) soils. Takimoto *et al.* (1976) found that fenitrothion was readily converted to aminofenitrothion in four different soils from Japan under flooded conditions.

Miyamoto (1977) studied the relative persistence of fenitrothion in four Japanese soils under flooded and non-flooded conditions. In two soils, the rate of degradation of fenitrothion was almost similar under both water regimes. But in the other two soils (Moriyama and Katano), soil submergence accelerated the degradation of fenitrothion. Thus, the half-life of fenitrothion was about

4 days in Moriyama and Katano soils under flooded conditions, as compared to 28 days in Moriyama soil and 22 days in Katano soil under non-flooded conditions. Furthermore, the accumulation of metabolites differed with moisture regime. In non-flooded soils, 3-methyl-4-nitrophenol and carbon dioxide were the major products of decomposition of fenitrothion, while aminofenitrothion was formed as the major metabolite in all flooded soils.

In some flooded soils 50–66% of fenitrothion applied was converted to aminofenitrothion within 7 days. According to a recent study in our laboratory, degradation of fenitrothion in five tropical soils (from India) proceeded more rapidly under flooded conditions than under non-flooded conditions (Adhya *et al.*, 1987). The half-life of fenitrothion in five soils was 3.9, 6.6, 5.6, 5.4, and 10.9 days under flooded conditions, as compared to the corresponding values of 4.4, 10.5, 15.4, 20, and 97 days under non-flooded conditions. As in temperate soils, aminofenitrothion accumulated in three of the five tropical soils under flooded conditions, while 3-methyl-4-nitrophenol was the major metabolite in all non-flooded soils. These incubation studies under well-defined laboratory conditions would suggest identical rates and pathways of degradation of fenitrothion in tropical and temperate soils; but under actual field conditions, its degradation may be faster in the hot environment of the tropics than in cooler climates of the temperate region.

Diazinon is yet another organophosphorus insecticide widely used in rice culture. This insecticide lost its efficacy after regular and intensive use of three or more years in tropical rice paddies of the Philippines (IRRI, 1970) and Bangladesh. Likewise, in a recent bioassay study from India (Rao and Rao, 1984), brown planthoppers were released on potted rice plants at 2 days after one, two, three, four, and five applications of granular diazinon (at 1.5 kg a.i./ha at 30-day intervals) to the soil. The efficacy of diazinon in controlling brown planthoppers decreased progressively with successive applications, the mortality being 100% after the first application, 33% after the second application, and 0% after the third application.

In a study on the mechanism of this phenomenon, diazinon was found to disappear within 3–6 days after its incubation with paddy water from rice fields (three locations in the Philippines) that had been previously treated with diazinon (Sethunathan and Pathak, 1972). But the loss of this insecticide from water from fields with no history of diazinon use was negligible even after 20 days. The diazinon-degrading factor, found in paddy water from diazinon-treated rice fields, was inactivated following autoclaving. Moreover, a *Flavobacterium* sp. ATCC 27551, isolated from paddy water samples that had been previously treated with diazinon, showed an exceptional capacity to hydrolyse diazinon and then metabolize its hydrolysis product, 2-isopropyl-4-methyl-6-hydroxypyrimidine to CO₂ (Sethunathan and Yoshida, 1973c).

Undoubtedly, intensive use of diazinon in Philippine rice fields has eventually led to a build-up of diazinon-hydrolysing soil microbes under actual tropical

field conditions. Also, repeated field application to a temperate soil from England led to accelerated degradation of diazinon (Forest *et al.*, 1981). A *Flavobacterium* sp. isolated from this conditioned soil hydrolysed diazinon. This would, at least in part, explain the decreased efficacy of diazinon in rice fields after its repeated applications.

Growing cells (Adhya *et al.*, 1981b) and phosphotriesterases (Brown, 1980) of *Flavobacterium* sp. 27551, isolated from diazinon-treated rice field in Philippines, hydrolysed both diethyl (diazinon, parathion) and dimethyl (methyl parathion and fenitrothion) phosphorothioates. The *Flavobacterium* sp., isolated from temperate soil, hydrolysed diazinon and parathion (Forest *et al.*, 1981). The *Pseudomonas* sp. 29353, isolated from an Indian soil enriched with parathion, hydrolysed both diethyl phosphorothioates (parathion and diazinon), despite the differences in ring moiety, but not the dimethoxy compounds, methyl parathion and fenitrothion. The ability of *Pseudomonas* sp. to hydrolyse parathion and diazinon, but not methyl parathion, suggests that the alkyl constituent attached to phosphorus is more important than the aromatic portion in determining the susceptibility of these phosphorothioates to bacterial hydrolysis. Thus, these versatile bacteria, *Flavobacterium* sp. in particular, isolated from tropical agricultural soils are equipped with powerful hydrolases for decontamination of systems polluted with parathion and related organophosphorus insecticides.

5.2.4 CARBAMATES

Until the mid-1960s, carbamate insecticides were seldom used in India, and probably not in any other tropical countries. In recent years, however, carbamate pesticides are used increasingly in the tropics for controlling specific pests not controlled by organochlorines and organophosphates. For instance, the N-methylcarbamates, carbaryl and carbofuran, are used increasingly as the most effective insecticides against brown planthoppers (*Nilaparvata lugens* Stål.), a major pest of rice in the tropics and subtropics. In India, carbaryl is probably second only to hexachlorocyclohexane in terms of the estimate for pesticide use during the period 1977–82 (Krishna Murti and Dikshith, 1982). Since carbamate use in tropical countries is more recent, the metabolism of carbamate pesticides under tropical conditions is less well understood than that of organochlorines and organophosphates.

Reports on the persistence of carbaryl in flooded soil are contradictory. Carbaryl disappeared completely from the non-sterilized suspension of a Philippine soil within 8 days, as based on UV-absorption spectral analysis of the supernatant of the soil suspension (IRRI, 1966). However, in a flooded alluvial soil from Malaysia, Gill and Yeoh (1980) showed a half-life of about 7 weeks. Carbaryl was more persistent in an acid sulphate soil than in the alluvial soil. The accumulation of the hydrolysis product, 1-naphthol, correlated with

the disappearance of carbaryl. There are reports of more rapid (Venkateswarlu *et al.*, 1980; Rajagopal, 1984) degradation of carbaryl in tropical soils under flooded conditions than under non-flooded conditions. In another study (Brahmaprakash, 1984), soil degradation of carbaryl occurred at almost identical rates under both water regimes. Degradation occurred both in sterile and non-sterile soils, but more rapidly in the latter.

There is considerable literature on the metabolism of carbaryl and/or 1-naphthol in cultures of microorganisms isolated from temperate environments and in microbial enzyme systems (Bollag and Liu, 1971; Bollag, 1981). A few instances of degradation of carbaryl in pure and mixed cultures of microorganisms isolated from tropical soils have been reported. A strain of *Achromobacter* sp. converted carbaryl in a mineral salts medium to 1-naphthol, hydroquinone, catechol, and pyruvate (Sud *et al.*, 1972). Also, this bacterium grew well with all the four metabolites as sole source of carbon.

In a more recent study (Rajagopal *et al.*, 1983; Rajagopal, 1984), suspensions from three (an alluvial, a laterite, and a sodic) tropical flooded soils, that had been previously treated three times with carbaryl or 1-naphthol, effected a more rapid degradation of carbaryl in a mineral salts medium than did the suspensions from the same soils never before exposed to carbaryl. This indicated enrichment of soils with carbaryl-degrading microorganisms following application of not only carbaryl but also its hydrolysis product, 1-naphthol. Also, bacteria isolated from these soil enrichments showed exceptional capacity to degrade carbaryl in a mineral salts medium (Rajagopal *et al.*, 1984c). Interestingly, degradation of carbaryl by soil enrichments and bacterial cultures was more pronounced in the absence than in the presence of ammonium nitrogen, possibly due to the preferential utilization of the inorganic nitrogen by the microorganisms. Evidently, an N-free environment is especially suitable for the proliferation of microorganisms that degrade nitrogenous pesticides, such as carbaryl.

In yet another study (Hirata *et al.*, 1984), repeated applications of carbaryl to grey humic and red yellow latosol increased the rate of degradation of carbaryl, possibly due to a rapid increase in the number of microorganisms using the pesticide as a substrate. Such microbial enrichment after carbaryl application suggests that microbial degradation of carbaryl is of great significance in neutral soils. Evidence suggests some microbial degradation of carbaryl even in an alkaline soil (sodic) where chemical hydrolysis is considerable (Rajagopal *et al.*, 1983).

Enrichment cultures and pure cultures of bacteria from carbaryl-amended soils degraded not only carbaryl but also carbofuran with almost equal ability. The degradation of carbaryl by all soil enrichments and bacterial cultures proceeded essentially by hydrolysis to 1-naphthol. Within 5 days of incubation with soil enrichment cultures, 1-naphthol and an unidentified metabolite were formed from carbaryl (Rajagopal, 1984). 1-Naphthol was metabolized further, but slowly, to 1,4-naphthoquinone by a *Bacillus* sp. Conversion of ring ^{14}C in

carbaryl to $^{14}\text{CO}_2$ or other volatiles by enrichment cultures and pure cultures of bacteria (Rajagopal *et al.*, 1984c) was negligible, even after 40 days of incubation. Consequently, most of the ring ^{14}C in carbaryl accumulated in the medium.

In recent years, there has been considerable concern over the environmental hazard from the intensive use of carbofuran in flooded rice paddies in the tropics and subtropics. Carbofuran degradation in some tropical soils was faster under flooded conditions than under non-flooded conditions (Venkateswarlu *et al.*, 1977; Li and Wong, 1980; Rajagopal, 1984). Furthermore, the degradation of carbofuran in flooded soils was more rapid under undisturbed conditions (predominantly anaerobic) than under aerobic conditions provided by shaking (Venkateswarlu and Sethunathan, 1978). Under continued anaerobiosis of undisturbed flooded soils, the hydrolysis product, carbofuran phenol, accumulated, but when the undisturbed soil was returned to an aerobic condition, carbofuran phenol decreased rapidly. The addition of rice straw also accelerated the hydrolysis of carbofuran to carbofuran phenol in predominantly anaerobic flooded soils (Venkateswarlu and Sethunathan, 1979).

Fluctuations in aerobic status and organic amendments alter the microbial activities in the soil and thereby influence the persistence of soil-applied carbaryl, carbofuran and their metabolites. The degradation of these carbamates in all soils proceeded by hydrolysis to 1-naphthol and carbofuran phenol, respectively, which showed recalcitrance to further degradation. Also, evolution of $^{14}\text{CO}_2$ from the ring ^{14}C in carbaryl and carbofuran (Venkateswarlu and Sethunathan, 1979; Rajagopal and Sethunathan, 1984) was negligible (less than 0.3% of the applied ring ^{14}C) in 40 days; during this period, 27% of the carbonyl ^{14}C was evolved as $^{14}\text{CO}_2$. Most of the ring ^{14}C in carbaryl and carbofuran accumulated in the soil as the hydrolysis products plus soil-bound residues (Rajagopal and Sethunathan, 1984).

In recent years, there has been increasing concern over the decreased efficacy of carbofuran in controlling insect pests in cornfields of temperate countries, viz. USA and Canada (Fox, 1983) and in flooded rice paddies of the Philippines in the tropics (IRRI, 1977). Two main groups of pesticides were affected by decreased efficacy in cornfields of the USA: carbofuran insecticides and thiocarbamate herbicides. This problem was aggravated by repeated use of the same pesticide in successive years. Research in temperate countries provided convincing evidence of accelerated degradation of carbofuran on its incubation with soil samples from fields with a 2–4 year history of continuous carbofuran use (Kaufman, 1983). Interestingly, accelerated degradation of carbofuran occurred in some, but not all, re-treated soil samples. Read (1983) found that carbofuran was degraded 600–1000 times faster in soil samples from Canadian cornfields previously treated with this insecticide than in soil samples from fields with no history of carbofuran use. Likewise, Felsot *et al.* (1981) reported

enhanced degradation of carbofuran in soil samples from cornfields in Illinois with a three-year history of continuous carbofuran use and reported a problem of a decreased efficacy of carbofuran.

In another study with a humic Mesisol from Canada, the decomposition of carbofuran was faster in re-treated soil than in soil with no history of carbofuran use (Greenhalgh and Belanger, 1981). No appreciable degradation of carbofuran occurred in 90 days in soil samples that had been sterilized before its addition; but where these sterile soil samples were inoculated with soils with a history of carbofuran use and then fortified with carbofuran, the insecticide disappeared almost completely in 30 days (Felsot *et al.*, 1981). Also, a *Pseudomonas* sp., isolated from re-treated soil, effectively degraded the insecticide in 30 days. Likewise, Read (1983) found that soil from re-treated cornfields lost its ability to degrade carbofuran when sterilized before the addition of the insecticide. According to these observations, accelerated degradation of carbofuran in re-treated soils was caused by soil microorganisms.

Evidence for a microbial role in the decreased efficacy of carbofuran in tropical rice fields is not conclusive. The persistence curves of carbofuran in a soil with and without a history of continuous carbofuran use were almost identical (Siddaramappa *et al.*, 1978; Venkateswarlu and Sethunathan, 1978). In another study (Rajagopal, 1984), carbofuran, applied to a soil, decreased to 14, 8, and 5% of the original level 40 days after one, two, and three applications, respectively. This slight increase in the rate of degradation of carbofuran after successive applications to the flooded soil does not suggest a distinct build-up of carbofuran-degrading microorganisms in the re-treated soil. However, when suspensions from the re-treated (viz. after three applications of carbofuran) and untreated soils were added to a mineral solution supplemented with carbofuran, the suspension from re-treated soil effected more rapid degradation of the insecticide than the suspension from the untreated soil (Rajagopal *et al.*, 1984b). Also, microorganisms isolated from these soil enrichment cultures were capable of degrading the insecticide (Rajagopal *et al.*, 1984b). This would suggest enrichment of microorganisms capable of degrading carbofuran after repeated applications of carbofuran or carbofuran phenol. It is not then clear why the degradation of carbofuran was not distinctly accelerated in the tropical soil after its repeated applications despite enrichment of carbofuran-degrading microorganisms.

The decreased efficacy of carbofuran insecticides in cornfields of the USA is analogous to the decreased efficacy of diazinon in controlling brown plant-hoppers in tropical rice fields of the Philippines, attributed, at least in part, to the build-up of diazinon-hydrolysing bacterium, *Flavobacterium* sp. ATCC 27551, in particular after repeated applications of the insecticide for seven consecutive seasons (Sethunathan, 1972; Sethunathan and Pathak, 1972; Sethunathan and Yoshida, 1973c). Carbamate and organophosphorus pesticides are short-lived and their dissipation is further hastened in a tropical environment.

This would necessitate more frequent application of these insecticides for effective pest control. However, such repeated applications, would, in turn, hasten the build-up of soil microbes that undermine the efficacy of these pesticides. Thus, the problem of reduced efficacy of pesticides associated with their rapid destruction by microorganisms may be more serious and widespread with short-lived carbamates and organophosphates than with more persistent pesticides.

5.2.5 RING CLEAVAGE REACTIONS

There is considerable evidence to indicate that ring cleavage reactions are retarded in predominantly anaerobic flooded soil not planted to rice. Less than 1–2% of the originally applied ring ^{14}C in HCH, parathion, diazinon, carbaryl, and carbofuran were evolved as $^{14}\text{CO}_2$ in 30–60 days from a flooded soil not planted to rice despite almost complete disappearance of the parent molecules (Sethunathan and Siddaramappa, 1978). Ring cleavage is an aerobic process mediated essentially by microorganisms. Increased soil aeration and intense microbial activity in the rhizosphere may accelerate ring cleavage reactions in a flooded soil planted to rice. Thus, in unplanted soil, less than 5.5% of the ring ^{14}C in parathion was evolved in 15 days under both flooded and non-flooded conditions (Reddy and Sethunathan, 1983a, 1983b). In soil planted with rice, 9.2% of the radio-carbon was evolved under non-flooded conditions and 22.6% under flooded conditions. Evidently, flooded soil planted with rice permits significant ring cleavage.

But not all pesticides undergo significant ring cleavage in flooded soil planted to rice. Evolution of $^{14}\text{CO}_2$ from ring ^{14}C in HCH, carbaryl, and carbofuran was negligible (less than 2% of original level) both in planted (to rice) and unplanted soils under flooded conditions (Brahmaprakash *et al.*, 1985; Figure 5.2.2). Despite slow ring cleavage, accumulation of soil-bound residues from gamma-HCH was negligible (less than 2.5% of original level), possibly because of the immediate volatilization of its degradation products, gamma-PCCH and gamma-TCCH, which are more volatile than gamma-HCH. Slow ring cleavage of carbaryl and carbofuran led to significant accumulation of ^{14}C as their hydrolysis products (1-naphthol or carbofuran phenol) and soil-bound residues both in planted and unplanted soils under flooded conditions (Brahmaprakash and Sethunathan, 1985).

5.2.6 CONCLUSIONS

We do not have comparative data for many pesticides on their persistence in temperate versus tropical soil environments. Even in limited instances, as for example HCH, where data have been generated by independent studies with tropical and temperate soils, a meaningful comparison is seldom possible,

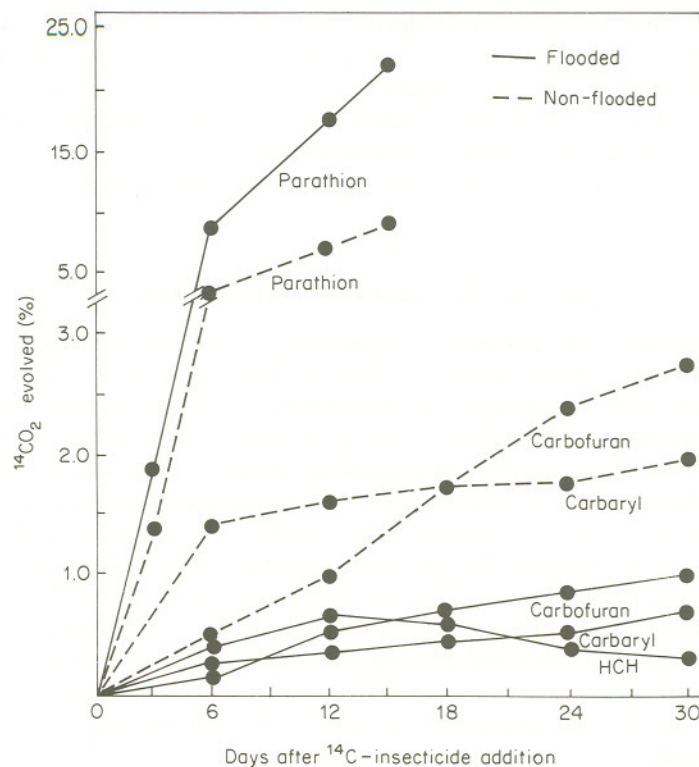


Figure 5.2.2 Cumulative $^{14}\text{CO}_2$ (percentage of the added ring ^{14}C) evolved from ring-labelled parathion (Reddy and Sethunathan, 1983a), hexachlorocyclohexane (HCH), carbofuran, and carbaryl (Brahmaprakash and Sethunathan, 1985; Brahmaprakash *et al.*, 1985) in a soil planted to rice under flooded and non-flooded conditions (Reproduced by permission of Elsevier Scientific Publishers B.V.)

because of several variables, such as soil type and experimental conditions. However, on the basis of the circumstantial evidence from soil persistence studies at different temperatures under laboratory conditions, most pesticides would undergo fairly rapid degradation under the high temperatures encountered in the tropics. There are also several reports of the rapid disappearance of several pesticides applied to tropical and subtropical agricultural soils under actual field conditions (Talekar *et al.*, 1977, 1983a, 1983b); but in most of these field studies only parent pesticide molecules were monitored.

Conclusions based on the monitoring of only parent pesticide molecules and not their degradation products can be misleading, since especially under hot and humid conditions of the tropics, substantial loss of pesticides can occur through phenomena like volatilization, lateral or vertical transport, and photodecomposition, besides microbial and chemical degradation. Available evidence indicates

that degradation pathways of pesticides may be identical in tropical and temperate conditions, but the rate of these degradation processes may be faster in the tropics.

For a meaningful generalization of pesticide behaviour in tropical versus temperate conditions, there is an urgent need to generate data on the fate of more pesticides in the tropical soil environment.

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