

# 5 BEHAVIOR OF PESTICIDES IN RICE-BASED AGROECOSYSTEMS: A REVIEW

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## 5.1. Introduction

Emphasis on agricultural production using modern techniques has focused attention on the problem of yield losses due to pests and the need for adequate protection of the crop. Pesticide application is currently the most widely practiced method of pest control in rice and rice-based cropping systems. Because of their toxic nature there is a general concern with the potential hazards of pesticides to humans and the environment.

The fate of pesticides applied in agricultural ecosystems is governed by the transfer and degradation processes and their interactions. Transfer is a physical process in which the pesticide molecules remain intact; it includes sorption-desorption, runoff, percolation, volatilization and absorption by crop plants or animals. Degradation is a chemical process in which pesticide molecules are split; it includes photodecomposition, microbiological decomposition, chemical decomposition, and plant detoxication. Transfer and degradation determine pesticide persistence or retention, its efficacy for pest control, as well as its potential for contamination of the soil and water resources.

Growing evidence indicates that pesticides are present in food grown on the land in surface and subsurface bodies of water and in the atmosphere. Research

has established the toxic effects of some pesticides on fish and other aquatic animals, on birds and other wildlife, and on human health. There is therefore a growing interest in understanding the processes relevant to the transport, transformation, and retention behaviors of pesticides used in agricultural production systems.

This paper reviews the information on the fate of pesticides in rice-based agroecosystems with emphasis on wetland soils.

Early studies of the fate of pesticides in soils have dealt mostly with upland soils. The bibliographic review on microbial transformation and decomposition of pesticides by Hill (1978) includes 334 references, among which only six refer to flooded soils. Similarly, the review of microbial degradation of insecticides by Matsumura and Benezet (1978) lists 133 references but only ten on submerged soils.

During the 1970s, interest in pesticide fate in wetland rice soils developed, especially with the studies conducted by Sethunathan and his coworkers, who authored between 1969 and 1984 more than fifty papers on this topic. Work on microbial degradation of insecticides in flooded rice soils was reviewed by Sethunathan (1973a) and Sethunathan and Siddaramappa (1978). About 100 pesticide studies dealing with ricefields, rice soils, or organisms isolated from ricefields were published during the 1970s. The number falls to about fifty in the 1980s. Since 1990 very few pesticide studies have dealt with ricefields.

## **5.2. Pesticide Use in Wetland Rice Fields**

### *5.2.1. Pesticide Categories*

In most rice-growing countries, insecticides are the dominant class of pesticides used (Van der Valk and Koeman, 1988). In the Philippines, for example, 55 to 60 percent of the pesticides used before 1980 were insecticides, 20 to 25 percent fungicides, and 5 to 16 percent herbicides. However, herbicide use is increasing rapidly due to the escalating costs of labor in many areas (Moody, 1990). Molluscicides have recently been introduced in some rice-growing regions in Asia where golden snails (*Pomacea canaliculata*) have become a threat to rice seedlings.

### *5.2.2. Quantities of Pesticide Applied*

In recent years, pesticide use has increased more rapidly in developing countries than in the developed countries. This trend toward pesticide usage is a cause for concern (Moody, 1990).

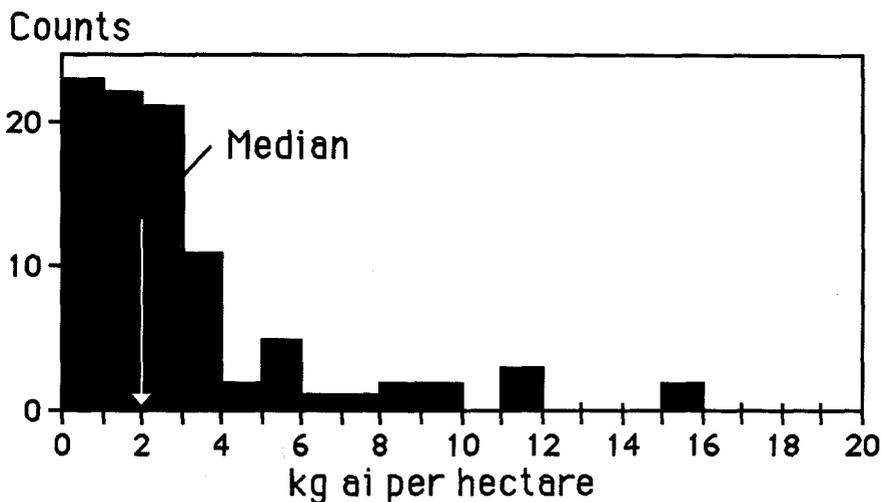


Figure 5.1. Histogram of the Average Recommended Doses of Ninety-Four Pesticides Tested for Their Microbiological Effects in Ricefields

**5.2.2.1. Recommended Application Rates.** Recommended level for field application (RFLA) of traditional pesticides range from a few hundred grams to a few kilograms (kg) active ingredient per hectare (ai/ha), with a median of about 2 kg (Figure 5.1). The median is higher for herbicides (2.5 kg ai/ha) than for fungicides (1.7 kg ai/ha) and insecticides (1.1 kg ai/ha) (Roger, 1990).

When interpreting the results of experiments on pesticide, it is important to appreciate that application rates do not necessarily equate with exposure concentration. The upper limit of the range of pesticide concentrations that can be expected in farmer fields after application can be calculated by assuming that pesticide is applied on a nonflooded soil and remains in its first two centimeters. In this case, 1 kg ai/ha corresponds to 10 parts per million (ppm) on dry soil basis (bulk density 0.5). A lower limit can be calculated by assuming an even distribution in 10 centimeters (cm) of water and 10 cm of puddled soil of a water-soluble pesticide. In this case, 1 kg ai/ha corresponds to 0.4 ppm. Field concentrations are probably closer to the lower level.

**5.2.2.2. Farmers' Behavior.** In irrigated rice farming using high-yielding varieties, chemical pesticide use is a common practice. However, rice farmers in developing countries frequently ignore recommended pesticide application regimes. Both excessive and reduced application have been reported.

Application can be excessive in term of quantity used per application, when

farmers apply more than the recommended dose, or in terms of unnecessary applications, especially when farmers use chemical pesticides in prophylactic applications expecting to prevent pest infestation or to keep the pest population low.

A survey conducted in 1989 by International Rice Research Institute (IRRI) in thirty-two farms of the Laguna area in the Philippines indicated a wide range of pesticide use in terms of formulation (twenty-one) and quantity. The total quantity of pesticide used during a cropping season in a field ranged from 0.5 to 2.5 kg ai/ha. Most values were between 1 and 2 kg ai/ha. The quantities of individual pesticides used per cropping season averaged 0.3 kg ai/ha and did not exceed 1 kg ai/ha. The values were often below the recommended dose (Roger et al., 1990).

### **5.3. Methods of Studying Pesticide Behavior in Rice Production System**

Many experiments studying the fate of pesticide in ricefield soils are small-scale laboratory experiments in test tubes or beakers. Microcosms and models have also been used. Field experiments are less numerous.

#### *5.3.1. Small-Scale Experiments*

Most studies of pesticide degradation in soil were performed as laboratory experiments with a few grams of soil. Under such conditions pesticide degradation might be underestimated because of

- The absence of the rhizospheric effect, which may enhance pesticide degradation;
- The absence of rice plants and wind, which may increase pesticide loss by volatilization;
- The absence of variations of environmental conditions (temperature, redox, light, wind, etc.); and
- The high pesticide concentrations sometimes used in such experiments, which may overestimate pesticide persistence because high concentrations slow down pesticide degradation as shown with trifluralin (Parr and Smith, 1973) or molinate (Deuel, Turner, Brown, and Price, 1978).

#### *5.3.2. Microcosms and Scale Models*

Several authors have tried to develop small-scale models (microcosms) of rice-fields or aquatic ecosystems to study the fate of pesticides. Such models offers an interesting alternative to field studies, which are often more expensive and difficult to control. Chen, Err-Lieh, and Chen (1982) used a microcosm including

rice plants and ten organisms (grasshopper, brown planthopper, mosquito larva, wolf spider, water flea, dragonfly naiad, giant duckweed, mosquito fish, algae, and snails) to study the fate of  $^{14}\text{C}$  labeled thiobencarb. However utilization of sand instead of soil in the model ecosystem might have biased the results. Tomizawa (1980) and Tomizawa and Kazano (1979) used a similar approach to study the persistence and bioaccumulation of several rice pesticides in the environment. Tejada and Magallona (1986) used a model ecosystem to study bioaccumulation of carbofuran in fish grown in a rice-fish system. Microcosms were also designed by Au (1980), Isensee, Kaufman, and Jones (1982), Lichtenstein, Liang, and Koeppe (1983), Seiber, McChesney, Sanders, and Woodrow (1986), Higashi and Crosby (1987) and Mostafa, El-Arab, and Zayed (1987) to study or predict the dissipation of various pesticides applied to flooded ricefields. Major characteristics of ricefield microcosm studies are summarized in Higashi (1987).

Microcosm studies may lead to erroneous conclusions if environmental conditions are not properly reproduced. Comparing molinate dissipation under field and microcosm conditions mimicking day-night light and temperature cycles, Higashi (1987) found only 15 percent difference in the estimations from both methods, which was acceptable. But in comparing bentazon dissipation under both diurnal cycle and constant light conditions in a microcosm, he found that the results gave opposite conclusions—namely, that it does and does not accumulate. He established that the field-mimicking microcosm experiment (diurnal light cycle) was closer to field observations.

### 5.3.3. *Field Trials*

Few field trials have been used for monitoring the persistence of pesticides. When several samples were collected in the same field, a high variability of the concentrations was observed; for example, determinations of propanil in four soil samples from the same field forty days after application ranged from less 0.01 ppm to 0.2 ppm (Kearney, Smith, Plimmer and Guardia, 1970). This high variability results, at least partly, from the importance of microbial activities in the degradation of pesticides and the aggregative distribution of microorganisms in the soil. Therefore, sampling strategies adapted to microbiological studies *in situ* (Roger, Jimenez, and Santiago-Ardales, 1991) must be used in pesticide persistence studies.

### 5.3.4. *Simulation Models*

Pesticide behavior in the ecosystem is very complex and determined by many variables and their interactions. Although the basic processes involved in their fate after application are established, it is difficult as well as expensive to adequately characterize them experimentally, taking account of the interactions,

over the range of physical conditions that are of interest. Therefore, the mathematical modeling technique using microcomputers has proved to be an attractive alternative for predicting various aspects of pesticide behavior. However, successful simulation modeling requires accurate mathematical formulation of the various component behaviors of applied pesticide and construction of the relational model that would adequately represent the processes governing pesticide behaviors. Much more research has to be done to achieve the progress needed in this area in order to allow development of comprehensive pesticide behavior models for practical use.

In recent years several simulation models have been developed to determine the fate of pesticide, ranging from pesticide spray behavior to pesticide retention in soil profile, leaching to groundwater, or degradation in freshwater bodies. These models are by no means simple to apply in all cases or universally applicable. Furthermore, the few well-tested models that are available were developed for important field crop systems of the temperate climate. Examples are the Bragg spray model (Bragg, 1981) for spray drift in pesticides applied by aircraft, the PRZM model (Carsel et al., 1984) to simulate vertical pesticide movement in the root zone or the unsaturated soil above water table, and the CREAMS model (Knisel, 1980) designed to determine runoff pesticide load from agricultural production systems. Since the ricefield ecosystem in wetland culture is quite unique, the applicability of the models to rice ecosystem is therefore often limited. However, with appropriate modifications some of the models could be adapted to the local ricefield conditions. A practical limitation of adapting and readily using most simulation models for ricefield ecosystems in Asia is the lack of data that are needed for parameter calibration.

Very few studies have been conducted on developing models to establish pesticide behavior in ricefields. Seiber, McChesney, Sanders and Woodrow (1986) calculated volatilization rates of MCPA, thiobencarb, and molinate from water using a computer model (EXAMS) and measured them in a laboratory chamber and in flooded ricefields. A fair to good correlation was obtained between EXAMS-calculated and chamber-measured rates for all three herbicides. Field-measured values correlated well with chamber measured rates for thiobencarb and molinate. For MCPA, field-measured values were much higher than expected for volatilization from water alone. In this case, the presence of plant and other surface residues in the field made the major contribution to measured volatilization.

#### **5.4. Decomposition of Pesticides in Wetland Soils**

As in any cultivated soil, the metabolism and effects of pesticides in ricefields depend on soil properties, climatic factors, the method of pesticide application,

and synergistic-antagonistic effects among pesticides and between pesticides and fertilizers. However, pesticide behavior in ricefields presents characteristics specific to wetland conditions. In particular, their degradation in tropical ricefields is favored by (1) temperatures and pH, which usually stabilizes in a range (6.7 to 7.2) favoring microbial activity (Ponnamperuma, 1972), and (2) reducing conditions caused by submersion and further accelerated by organic matter incorporation. This results in rapid detoxication of certain pesticides known to persist in aerobic environment (Sethunathan and Siddaramappa, 1978).

#### 5.4.1. *Mechanisms and Chemical Pathways of Pesticide Decomposition*

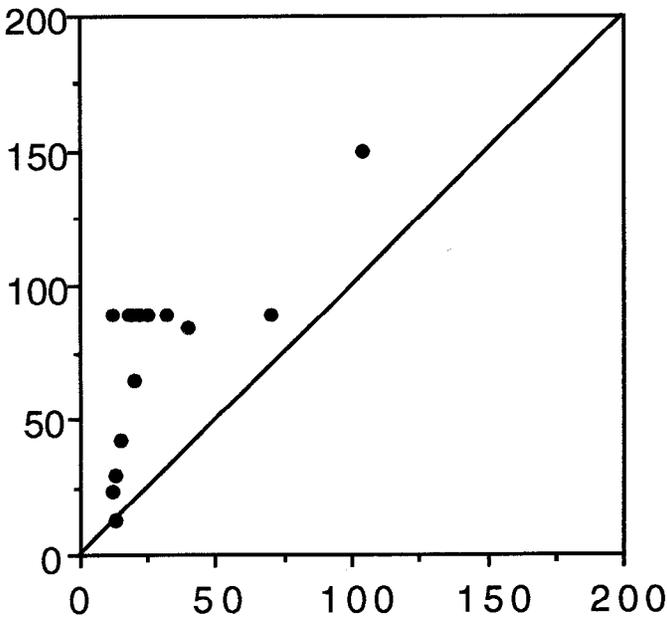
**5.4.1.1. Microbiological Decomposition.** A usually much faster degradation of pesticides in nonsterile than in sterilized (autoclaved) soils demonstrates the importance of their microbial degradation (Figure 5.2). Microbial involvement in pesticide degradation is also indirectly established by (1) an initial lag in degradation followed by a faster loss attributed to microorganisms adaptation, (2) an initial lag becoming shorter with repeated application of the same pesticide, due to the enrichment of the microflora in pesticide-degrading microorganisms, (3) inhibition of pesticide degradation after addition of antibiotics or bacteriostatics to soil-water cultures, and (4) increased decomposition after soil inoculation with enrichment cultures. Direct demonstration is done by the isolation of microorganisms that are able to degrade pesticides in pure culture (Adhya, Sudhakar-Barik, and Sethunathan, 1981b, 1981c; Rajagopal, BrahmaPrakash, and Sethunathan, 1984).

Pesticide-decomposing microorganisms isolated from ricefield soils belong to the genera *Arthrobacter*, *Bacillus*, *Clostridium*, *Flavobacterium*, *Micrococcus*, *Mycobacterium*, *Pseudomonas*, and *Streptomyces* (Table 5.1). Microorganisms can degrade pesticides using them as sole carbon source, through cometabolism, or by synergy. For example, Sethunathan (1972) reported one species (*Flavobacterium* sp.) that used diazinon as sole carbon source, five species degrading it by cometabolism (*Arthrobacter* sp., *Corynebacterium* sp., *Pseudomonas melophthora*, *Streptomyces* sp. and *Trichoderma viride*), and two species acting in synergy (*Arthrobacter* sp. + *Streptomyces* sp.).

The relative importance of microbial degradation varies considerably between soils and pesticides. The half-life of gamma BHC was about forty-five days in a nonsterilized soil and about eighty days in the same soil that had been sterilized (Raghu and MacRae, 1966). Trifluralin was almost not decomposed after twenty days in a sterilized soil while it had almost completely disappeared in the same unsterilized soil enriched with alfalfa meal (Parr and Smith, 1973).

In upland conditions, bacteria and fungi are considered to be mainly responsible

## Half-life in autoclaved soil (days)



## Half-life in nonautoclaved soil (days)

Figure 5.2. Stability of Thirteen Pesticides in Autoclaved and Nonautoclaved Soils

Source: Drawn from data by Agnihotri (1978); Funayama, Uchida, Kanno, and Tsuchiya (1986); Gowda and Sethunathan (1976); MacRae, Raghu, and Castro (1967); Nakamura, Ishikawa, and Kuwatsuka (1977); Raghu and MacRae (1966); Sethunathan and MacRae (1969); Siddaramappa, Tirol, and Watanabe (1979).

for pesticide transformations in soils. In wetland soils, fungi are involved (Rao and Sethunathan, 1974) but are probably less important, whereas microalgae might have a significant role. Sato and Kubo (1964) found that parathion was degraded within a few days in ricefields and that the presence of algae greatly accelerated the degradation rate.

Experiments in flasks have shown that the toxic effect of BHC, HCH, and carbofuran on axenic cultures of BGA was reduced by repeated inoculation and removal of the algae (Das and Singh, 1977; Kar and Singh, 1979). The mechanism of toxicity reduction was not elucidated; it could have been pesticide degradation by the alga, accumulation and removal with harvested algae, or spontaneous degradation of the pesticide.

Table 5.1. Pesticide Degrading Microorganisms Isolated from Ricefields

Pesticide	Microorganism	Reference
Benzene hexachloride	<i>Clostridium</i> sp.	— Sethunathan, Bautista, and Yoshida, 1969
Carbaryl	<i>Pseudomonas cepacia</i>	— Venkateswarlu, Chendrayan, and Sethunathan, 1980
Carbofuran	<i>Arthrobacter</i> sp.	— Rajagopal, Rao, Nagendrapa, and Sethunathan, 1984
Carbofuran	<i>Bacillus</i> sp.	— Rajagopal, Rao, Nagendrapa, and Sethunathan, 1984
Carbofuran	<i>Micrococcus</i> sp.	— Rajagopal, Brahmaprakash, and Sethunathan, 1984
Diazinon	<i>Arthrobacter</i> sp.	— Sethunathan and Pathak, 1971
Diazinon	<i>Arthrobacter</i> sp.	— Sethunathan, Adhya and Raghu, 1982
Diazinon	<i>Flavobacterium</i>	— Yoshida, 1975
Diazinon	<i>Flavobacterium</i> sp.	— Sethunathan, 1972
Diazinon	<i>Steptomyces</i> sp.	— Sethunathan and MacRae, 1969
Gamma BHC	<i>Clostridium rectum</i>	— Ohisa and Yamaguchi, 1978b
Gamma BHC	<i>Clostridium</i> sp.	— Sethunathan and Yoshida, 1973b
HCH	<i>Clostridium sphenoides</i>	— Heritage and MacRae, 1979
Heptachlor	<i>Clostridium</i> sp.	— Sethunathan and Yoshida, 1973b
Lindane	<i>Clostridium</i> sp.	— MacRae, Raghu, and Bautista, 1969
Metoxychlor	<i>Clostridium</i> sp.	— Sethunathan and Yoshida, 1973b
Parathion	<i>Bacillus</i> sp.	— Siddaramappa, Rajaram and Sethunathan, 1973
Parathion	<i>Bacillus</i> sp.	— Sudhakar-Barik, Siddaramappa and Sethunathan, 1976
Parathion	<i>Flavobacterium</i> sp.	— Sethunathan and Yoshida, 1973a
Parathion	<i>Pseudomonas</i> sp.	— Siddaramappa, Rajaram and Sethunathan, 1973
Parathion	<i>Pseudomonas</i> sp.	— Sudhakar-Barik, Siddaramappa and Sethunathan, 1976
Pentachlorophenol	<i>Mycobacterium</i> sp.	— Suzuki, 1983a, 1983b
Pentachlorophenol	<i>Pseudomonas</i> sp.	— Watanabe, 1973b
Pentachlorophenol	<i>Pseudomonas</i> sp.	— Suzuki, 1983a, 1983b

Rhizospheric bacteria may play a significant role in pesticide degradation. In an unplanted flooded soil, less than 5.5 percent of the  $^{14}\text{C}$  of labeled parathion was evolved as  $^{14}\text{CO}_2$  in two weeks whereas 22.5 percent was evolved in planted soil (Rajasekhar and Sethunathan, 1983a). However, a rhizosphere effect on pesticide decomposition is not due to microbiological activity only. Mineralization of parathion in the rhizosphere of rice was more pronounced at the seedling stage than at the maximum tillering and panicle initiation stages; the degree of rhizosphere effect depended on the rice variety and was related to the root oxydase activity in rice but not necessarily to the biomass of the plant (Rajasekhar and Sethunathan, 1983b).

**5.4.1.2. Nonbiological Decomposition.** Pesticide degradation observed in the absence of biological activity indicates that physical and chemical processes are also involved. Rao and Sethunathan (1979) highlighted the importance of chemical transformations catalyzed by redox reactions such as the iron redox system.

Photodecomposition at soil and water surfaces is also important, particularly when exposed to direct sunlight. Under laboratory conditions, butachlor exhibited 95 percent decomposition after twenty-four hours of exposure to light. *In situ*, marked differences in half-life, which varied from five days to 0.8 day, were attributed to changes in climatic conditions, temperature and light intensity (Chen, 1980).

The relative importance of nonbiological degradation varies with pesticides and environmental conditions. For various insecticides, it ranged from 30 to 90 percent of the degradation in soil in the presence of microflora (Agnihotri, 1978). Degradation of carbofuran in water was mainly by nonbiological processes and was related to the initial pH; but in soil, it was associated with microbial activities (Siddaramappa and Seiber, 1979).

Beside microbiological and chemical degradation-transformation, pesticides can disappear from the ricefield through volatilization (see Section 5.5.2) and plant detoxication. The structure of many organic pesticides are altered by resistant plants; even susceptible plants may metabolize small amounts of pesticides.

Several pathways of degradation-dissipation can affect a single pesticide. Their relative importance varies, depending on environmental conditions. For example, trifluralin is decomposed both by physicochemical and microbiological processes. Degradation pathways differ under aerobic and anaerobic conditions and decomposition is usually faster under anaerobic conditions. Depending on experimental conditions, physicochemical process (Probst and Tepe, 1969) or microbiological process (Parr and Smith, 1973) predominate. In the presence of ultraviolet radiations, trifluralin is rapidly photodecomposed. In addition, trifluralin can be extensively lost by volatilization depending on concentration, mode of application, and moisture content of the soil (Bardsley, Savage, and Walker, 1968). Volatilization was reduced in flooded soil conditions (Parr and Smith, 1973).

#### *5.4.2. Factors That Affect Pesticide Decomposition in Wetland Soils*

**5.4.2.1. Climatic Factors.** The loss of organic pesticides through processes involving volatilization, photodecomposition, and, more important, microbial degradation is expected to be more rapid under tropical and subtropical conditions than in temperate environment (Sethunathan, Adhya, and Raghu, 1982).

Higher temperature in tropical areas might favor both microbial and chemical decomposition. Gamma HCH was shown to decompose faster at 35°C than at 25°C in a flooded soil (Yoshida and Castro, 1970). High temperature decreases adsorption and favors desorption of pesticides, which may result in higher amounts of pesticides dissolved in soil water and faster dispersion (Guenzi and Beard, 1976).

Diurnal variations in light intensity and temperature can lead to marked variations in photosynthetic activity in floodwater, resulting in water pH changes marked as two pH units within a day. Floodwater pH changes favor chemical decomposition of pesticides as reported for carbofuran (Seiber et al., 1978; Siddaramappa et al., 1978). Carbofuran loss due to hydrolysis was over 700 times more rapid at pH10 than at pH7.

In rainfed ricefields, soils subjected to alternate periods of flooding and drying, resulting in successions of microflora dominated aerobic and anaerobic microorganisms, might provide conditions favorable for more extensive decomposition by microorganisms. Sethunathan (1972) showed that diazinon was hydrolyzed in flooded soils, but the ring portions of its hydrolysis products were open only under aerobic conditions following anaerobiosis.

**5.4.2.2. Anaerobiosis: Wetland Versus Upland Conditions.** The comparison of pesticide stability in wetland and upland conditions (Figure 5.3) often shows a longer persistence in nonflooded soils than in flooded soils (Watanabe, 1973a; Sethunathan and Siddaramappa, 1978). Among organochlorine insecticides, DDT, DDD, methoxychlor, and heptachlor degraded faster in flooded soil than in upland soil; DDD was found to accumulate in DDT-treated flooded soil; and endrin was degraded only in flooded soil (Castro and Yoshida, 1971). As summarized by Sethunathan, Adhya, and Raghu (1982), while gamma HCH persisted for at least two years in aerobic upland soils, it reached nonsignificant levels (less than 0.02 ppm) within twenty to thirty days in submerged soils even after high repetitive applications of a total amount of 48 kg ai within four successive cropping seasons.

The faster pesticide degradation in wetland soils is at least partly due to a relation between soil redox (Eh) and pesticide degradation. A study of the relationship between Eh and the rate of trifluralin degradation, using a system for controlling redox potential in soil suspensions, indicated that O<sub>2</sub> exclusion by soil flooding initiated rapid trifluralin degradation only when the Eh decreased below a critical range between +150 and +50 mV (Willis, Wander, and Southwick, 1974). Gamma and beta isomers of HCH decomposed rapidly in nonsterile soils capable of attaining redox potentials of -40 to -100 mV within twenty days after flooding (Siddaramappa and Sethunathan, 1975; Sethunathan et al., 1976). Degradation was slow in soils low in organic matter and in soils with very low

## Half-life in flooded soil (days)

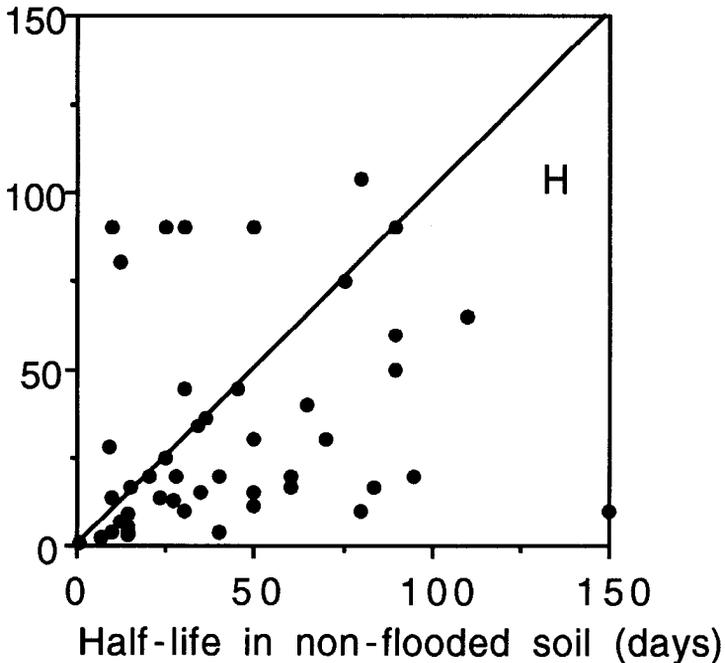


Figure 5.3. Stability of Thirty-Six Pesticides in Flooded and Nonflooded Soil

Source: Drawn from data by Agnihotri, 1978; Arita and Kuwatsuka, 1991; Castro and Yoshida, 1971; Ferreira and Raghu, 1981; Funayama, Uchida, Kanno, and Tsuchiya, 1986; Probst and Tepe, 1969; Probst et al., 1967; Rajaram and Sethunathan, 1976; Reddy and Sethunathan, 1983; Sethunathan, 1984; Sethunathan and Siddaramappa, 1978; Sethunathan and Yoshida, 1973c; Tomizawa, 1975; Tomizawa, Uesugi, Ueyama, and Yamamoto, 1976; Venkateswarlu, Gowda, and Sethunathan, 1977; Wang and Broadbent, 1973; Yoshida and Castro, 1970; Yoshida, 1975; Yoshida and Castro, 1975.

pH and positive Eh after several weeks of flooding (Sethunathan et al., 1976). A low or negative Eh also favored the degradation of DDT (Guenzi, Beard, and Viets, 1971), endrin (Gowda and Sethunathan, 1977), and toxaphene (Parr and Smith, 1976).

Pesticide degradation can be very rapid in prereduced soils as shown with parathion which exhibited 48 to 86 percent disappearance when shaken for five seconds with reduced soil (Wahid, Ramakrishna, and Sethunathan, 1980).

Sethunathan et al. (1980) suggested that redox potential, reducing capacity and certain reduction reactions, assayed, for example, in terms of nitrate disappeared or reduced iron formed, could be used as simple and suitable indicators of the pesticide-degrading capacity of anaerobic systems. Dehydrogenase activity

is well pronounced in predominantly anaerobic flooded soil and may have the obvious advantage over the  $^{14}\text{CO}_2$  evolution technique as an assay for the pesticide-degrading capacity of anaerobic systems.

Organic matter incorporation, which hastens the drop in Eh favors pesticide degradation (see Section 5.4.2.3). However, some pesticides may reduce the drop in Eh of rice soils, as observed with HCH by Pal, Misra, and Sethunathan (1980).

Sethunathan and Siddaramappa (1978) suggested that the alternate oxidation and reduction processes in intermittently flooded soils may favor degradation of pesticides. Brahmaaprakash, Reddy, and Sethunathan (1985) observed that the degradation of anaerobically unstable HCH isomers in the rice rhizosphere was not retarded by the possible aeration of a flooded soil by roots.

Some reports indicate no difference in degradation in upland and flooded conditions as observed for chlordane and dieldrin, which persisted for at least three months in both upland and submerged conditions (Castro and Yoshida, 1971). Similar findings have been reported for carbaryl (Rajagopal, Rao, Nagendrapa, and Sethunathan, 1984).

In some cases a longer persistence of pesticides was observed under flooded conditions than under upland conditions, as for benthocarb (Nakamura, Ishikawa, and Kuwatsuka, 1977), phorate (Walter-Echols and Lichtenstein, 1978), aldrin (Castro and Yoshida, 1971) and molinate, oxidation of which drastically decreases as Eh becomes lower than 100 mV (Deuel, Turner, Brown, and Price, 1978). Pesticide losses by volatilization can also be retarded in flooded environments, as shown for trifluralin (Parr and Smith, 1973).

The mechanisms of degradation-transformation differ in wetland and upland conditions; the same compound may be degraded through different pathways depending on the redox conditions. For example, trifluralin degrades by a pathway involving sequential dealkalination of propyl groups in aerobic conditions, and by a pathway involving initial reduction of the nitro groups in anaerobic conditions (Parr and Smith, 1973). In flooded conditions, the process of reductive dechlorination has been demonstrated for DDT, hydrolysis for diazinon and parathion, and nitro-group reduction for parathion. Dehydrochlorination (DDT), ring cleavage (IMHP), and epoxidation (aldrin and heptachlor) are apparently blocked or less favored in oxygen-depleted flooded soil (Sethunathan, 1972; Hill, 1978).

**5.4.2.3. Soil Factors.** The degradation rate of a given pesticide can markedly differ among soils. In a study of the fate of endrin in eight soils from India, Gowda and Sethunathan (1976) found percentages of persistence twenty-five days after application to average sixty-two, ranging from twenty-three to ninety-nine. A laboratory comparison of the degradation rate of  $^{14}\text{C}$ -labeled pyrazoxyfen in five rice soils from Japan under upland (50 percent of the maximum water-

holding capacity) or flooded (covered with one cm of water) conditions showed a faster degradation in the mineral soils (half-life: three to five days) than in the humic volcanic ashes (half life: five to thirty-four days) (Arita and Kuwatsuka, 1991). Among soil properties influencing pesticide degradation, pH and organic matter content are most often reported, but cation-exchange capacity, C/N ratio, and water-holding capacity are also involved (Arita and Kuwatsuka, 1991). On the other hand, no marked differences in the degradation rates of benthocarb were observed among three soils differing by their clay content (5 to 23 percent), pH (5.2 to 6.1), total C (1.8 to 7.9 percent) and CEC (14 to 40) (Nakamura, Ishikawa, and Kawatsuka, 1977).

The degradation of some pesticides is affected by soil pH. Sethunathan, Adhya, and Raghu (1982) presented several examples indicating that both alkaline and acidic conditions could enhance the decomposition of specific pesticides or groups of pesticides. They indicated that organophosphates and carbamates are more affected by soil pH than organochlorine insecticides. Aldicarb degradation was rapid in neutral soil, much slower at pH near 6.0, and greatly retarded at pH lower than 5.6 (Read, 1987).

The breakdown of pesticides in soil with low pH may be retarded because they have a high anion exchange capacity and therefore would tend to adsorb more pesticides than soils of high pH do (Edwards, 1974). Bailey, White, and Rothberg (1968) concluded that all organic herbicides tested were adsorbed more by an highly acid clay soil than a near neutral soil. Microbial degradation of carbofuran in these soils was the slowest in soil with the lowest pH (Siddaramappa, Tirol, and Watanabe, 1979).

Several reports indicate that pesticides are degraded slowly in acid sulphate soils. This was observed for gamma and beta BHC (Siddaramappa and Sethunathan, 1975), endrin (Gowda and Sethunathan, 1976), and carbofuran (Venkateswarlu, Gowda, and Sethunathan, 1977). In an acid sulfate soil, carbofuran exhibited a lag of about twenty days before degradation started (Venkateswarlu and Sethunathan, 1984). Carbaryl was more persistent in an acid sulfate soil (pH 3.7) than in other acid soils (pH 4.2 to 4.8) (Gill and Yeoh, 1980). Low pesticide degradation rates in acidic soils, particularly in acid sulphate soils, are commonly attributed to low bacterial activity. However, other factors may also be involved. Wahid and Sethunathan (1979) observed that hydrogen sulphide, the end product of sulfate reduction, which is frequent in such soils, was involved in the degradation of parathion.

Liming flooded-anaerobic acid soils was reported to cause a rapid conversion of DDT to TDE (Parr and Smith, 1974) but had no significant effect on the degradation of BHC (Siddaramappa and Sethunathan, 1975) and endrin (Gowda and Sethunathan, 1976).

Soils rich in organic matter often have a high microbiological activity, which

favors pesticide degradation. Organochlorine insecticides were found to degrade faster in soils with high organic matter content (Castro and Yoshida, 1971). In acid rice soils of Kerala, India, Sethunathan (1973b, 1973c) observed that parathion degraded faster in the soil that had a higher organic matter content. However, organic matter was found to be the most prominent soil factor conditioning sorption of pesticides in soil (see Section 5.5.1).

Several reports show that organic matter incorporation, which increases microbial activity and hastens the drop in redox potential in flooded soils, favors pesticide degradation. This was observed for straw incorporation (Adhya, Sudhakar-Barik, and Sethunathan, 1981a; Chopra and Magu, 1986; Gowda and Sethunathan, 1976; Lee, 1981; Siddaramappa and Sethunathan, 1975; Venkateswarlu and Sethunathan, 1979) as well as for green manure incorporation (Ferreira and Raghu, 1981; Parr and Smith, 1973). However, Castro and Yoshida (1974) observed this effect only when soil organic matter was low. Applications of rice straw to a flooded soil inoculated with parathion-hydrolysing enrichment culture inhibited the hydrolysis of the insecticide; the inhibitory factor was not formed in rice straw-amended flooded soils incubated at 50 and 75 percent moisture levels (Rajaram, Rao, and Sethunathan, 1978).

**5.4.2.4. Water Management and Method of Pesticide Application.** In uplands, pesticide remains at the soil surface until cultivation or watering incorporates them into the soil. In wetlands, a faster dilution can be expected, with variations depending on solubility and surfactants used. Pesticides can be sprayed, applied in the floodwater, incorporated into the soil, or used for dipping rice seedling at transplanting. Water management and the method of pesticide application might affect pesticide persistence and decomposition with regard to dilution and movements in the soil, but little information is available on this aspect.

The persistence of carbofuran in the soil was increased to about sixty days, and its concentrations in floodwater reduced by its incorporation at a depth of about 3 cm (Siddaramappa, Tirol, and Watanabe, 1979) or by its placement in gelatin capsules in the root zone (Siddaramappa and Seiber, 1979). A much faster dissipation was observed when seedling roots were soaked in carbofuran solution (Seiber et al., 1978). Similar observations were made for chlormediform (Aquino and Pathak, 1976).

Pesticide applied to the rice canopy is less subjected to microbial decomposition than when applied to the soil; however it has been shown that microorganisms present in the phyllosphere may contribute to pesticide decomposition (Rajagopal, BrahmaPrakash, and Sethunathan, 1984).

**5.4.2.5. Pesticide Concentration.** Pesticides applied at high concentrations seem to decompose more slowly than when applied at low concentrations.

Trifluralin at 200 ng/ $\mu$ l had a negligible rate of photodecomposition after forty days, compared with a half-life of about twenty days when applied at concentrations between 1 and 0.1 ng/ $\mu$ l (Parr and Smith, 1973). Molinate also persisted longer in plots treated at an excessive rate (Deuel, Turner, Brown, and Price, 1978).

**5.4.2.6. Effects of Combined Pesticides.** When two pesticides are applied simultaneously, one can inhibit the microorganisms responsible for the degradation of the other or modify the physicochemical conditions in a way that reduces its degradation. This was observed for *Clostridium rectum*, a BHC decomposer isolated from a ricefield soil, whose growth and BHC decomposing ability were inhibited by pentachlorophenol (Ohisa and Yamaguchi, 1978b). Similarly, benomyl applied in combination with parathion increased the persistence of generally short-lived parathion by inhibiting microbial hydrolysis and nitro group reduction (Sudhakar-Barik and Sethunathan, 1979). Benomyl also inhibited nitrification, iron reduction and the drop in the redox potential in the flooded soil: after twenty-four days of incubation Eh was  $-20\text{mV}$  in the control and  $+100\text{mV}$  in the treatment receiving 5 ppm benomyl, which contributed to reduced parathion decomposition (Sethunathan et al., 1980). In a model ecosystem, combination of methyl parathion with atrazine substantially decreased the degradation of both pesticides in the roots of rice and increased their persistence in water and soil (Au, 1980). However, soil incorporation of benthocarb with simetryne, CNP or propanil had no significant effect on the degradation rate (Nakamura, Ishikawa, and Kuwatsuka, 1977) and the persistence of parathion was not affected by simultaneous addition of HCH or 2,4-D (Sudhakar-Barik and Sethunathan, 1979).

**5.4.2.7. Effect of Fertilizers.** N fertilizer application may affect pesticide persistence but data are too scarce to draw general conclusions. The addition of ammonium nitrogen to a mineral medium retarded the degradation of the nitrogenous pesticide carbaryl by soil enrichment cultures (Rajagopal, Brahmaprakash, and Sethunathan, 1983). Ammonium sulphate and urea increased the persistence of carbaryl in a flooded laterite soil with a low nitrogen content (0.04 percent), but not in an alluvial soil with a higher nitrogen content (0.11 percent) (Rajagopal and Sethunathan, 1984). Applications of potassium nitrate or ammonium sulphate to a flooded soil inoculated with parathion-hydrolysing enrichment culture, inhibited the hydrolysis of the insecticide (Rajaram, Rao, and Sethunathan, 1978). Degradation of disulfon and phorate in soil alone was also slightly slower than when fertilizer was added; however, *in situ* degradation was faster when fertilizer was applied because of a better plant growth in the treated plots (Agnihotri, 1978). The application of ammonium sulphate and urea showed little

influence on the persistence of carbofuran in a Philippine flooded rice soil (Maahas clay) with a high nitrogen content (Siddaramappa and Seiber, 1979).

**5.4.2.8. Effect of Repeated Applications on Decomposition.** Repeated application of the same pesticide has been reported to enhance the growth of the related specific decomposing microorganisms and cause the rapid inactivation of the pesticide. A second application of gamma-BHC to a non-sterilized soil fifty-five days after the first one showed a faster degradation of the pesticide: half life was about eighteen days at the first application and twelve days at the second application (Raghu and MacRae, 1966). Diazinon persisted for about fifteen days in a flooded soil (pH 6.6) that had been treated previously with this insecticide; but it persisted for about sixty days in a soil that had never been exposed to diazinon (Sethunathan, 1972). Two successive annual applications of aldicarb, as subsurface band-in-row treatments at 4 kg ai/ha in the same field, resulted in the development of microorganisms that rapidly broke down aldicarb and accelerated its degradation in soil and water (Read, 1987). In a laboratory experiment with enrichment cultures from soil-water mixtures, the time needed for the breakdown of 50 ppm aldicarb applied repeatedly was eighty days for the first application, fourteen days for the fifth application, and three days for the tenth application (Read, 1987).

Several bacteria having the ability to degrade a given pesticide were isolated from soils or water of fields previously treated with the same pesticide. A *Flavobacterium* sp., isolated from water of a diazinon-treated ricefield, had exceptionally high capability to metabolize diazinon as its sole carbon source (Sethunathan, 1972; Sethunathan and Pathak, 1971). Similarly, Sudhakar-Barik, Siddaramappa, and Sethunathan (1976) isolated a *Pseudomonas* sp. and *Bacillus* sp. that were able to decompose nitrophenols from parathion-amended flooded soil. A substantial portion (23 percent for *Pseudomonas* sp. and 80 percent for *Bacillus* sp.) of radioactivity applied as p-nitrophenol was accounted for as  $^{14}\text{CO}_2$  at the end of a seventy-two-hour period. Watanabe (1973b, 1977) isolated PCP-decomposing and PCP-tolerant bacteria from soils and observed a 1,000-fold difference in the number of PCP-decomposing microorganisms between treated and untreated soil (Watanabe, 1978).

Enrichment cultures from soil repeatedly treated with pesticide have been used to isolate carbofuran-degrading bacteria, but even these cultures exhibited a lag in the degradation of carbofuran (Rajagopal, Brahmaprakash, and Sethunathan, 1983).

However, there are also reports indicating that repetitive application of pesticides did not lead to the buildup of the degrading microflora. This was reported in laboratory experiments with carbofuran (Siddaramappa et al., 1978; Venkateswarlu and Sethunathan, 1978) and benthocarb (Nakamura, Ishikawa,

and Kuwatsuka, 1977). Also Ohisa and Yamaguchi (1978a, 1978b) observed that enrichment of soil populations of *Clostridium rectum* (a bacterium isolated from ricefield soil that degrades BHC by a cometabolic process) was not caused by BHC application but by the addition of peptone.

Repeated application of pesticide has also been reported to cause changes in the metabolic pattern of pesticide decomposition (Sudhakar-Barik, Wahid, Ramakrishna, and Sethunathan, 1979). The principal metabolic pathway for the insecticide parathion shifted from nitro group reduction to hydrolysis on the repeated additions of parathion to a flooded soil. A similar result was obtained when p-nitrophenol, a parathion hydrolysis product, was applied, showing the enrichment of a population capable of degrading a parent molecule on application of the primary product of its metabolism. Both nitro group reduction and hydrolysis are cometabolic reactions; the buildup of parathion-hydrolysing microorganisms after parathion additions was at the expense of the product of the primary cometabolic hydrolysis, p-nitrophenol (Sethunathan et al., 1980).

Changes in degradation pathways can be detrimental. For example, benthocarb is generally detoxified by hydrolysis, but its repeated application to flooded soil favored the multiplication of anaerobic bacteria that decompose benthocarb by reductive dechlorination, resulting in the formation of a phytotoxic compound detrimental to rice (Moon and Kuwatsuka, 1984).

## 5.5. Pesticide Movements in Wetland Ricefields

After application, pesticides begin to disappear from the target area either by physical movement by the action of air or water, or by degradation (Taylor and Spencer, 1990).

Pesticide movements include adsorption/desorption by soil, volatilization, diffusion, percolation, runoff, and adsorption by plants and animals.

### 5.5.1. Adsorption-Desorption by Soil

Adsorption-desorption is a dynamic process in which molecules are continually transferred between the bulk liquid and solid surface (Koskenen and Harper, 1990). Adsorption is the binding of the pesticide molecules by the surface of the treated soil, whereas desorption implies detachment of the molecules to the liquid medium. The strength of the adsorption bond depends on the properties of both the pesticide and the soil. Adsorption-desorption of pesticides largely determines the quantity of pesticide available for biological interactions in soil and water. The organic matter content and the amount of colloidal materials in

the soil are major factors influencing pesticide sorption and persistence in soil. Higher amounts of colloidal materials increase persistence due to more adsorption surface area.

The classical method for studying sorption has been to shake  $^{14}\text{C}$ -labeled pesticide with a soil suspension for a short time (1 to 2 hrs) and to measure supernatant pesticide after centrifugation. Using this method, Sethunathan et al. (1980) found sorption accounting for 40 to 95 percent of applied pesticides. Between 60 and 70 percent of carbofuran added to three soils was recovered immediately after mixing the pesticide with the soil (Venkateswarlu, Gowda, and Sethunathan, 1977). Carbofuran recovery just after mixing with an alluvial soil was 57 percent in the control and 52 percent when the soil was enriched with 0.5 percent straw (Venkateswarlu and Sethunathan, 1979). Empirical relationships have been established by some researchers between extent of adsorption and organic matter content. A logarithmic relation between parathion sorption and organic matter content was reported by Wahid and Sethunathan (1978). Comparing rice soils of Tamil Nadu, India, Saivaraj and Venogupal (1978) found that mephosfolan persisted longer in clay soil containing a higher organic matter than in sandy soils.

In soils poor in organic matter, free iron oxide and clay might be related to pesticide sorption but the correlation has not been consistently observed. The correlation was significant with parathion and gamma BHC, but not with alpha BHC (Sethunathan et al., 1980).

Adsorption may also take place during the metabolism of pesticides in flooded soils. Katan, Fuhremann, and Lichtenstein (1976) reported that the decrease of extractable  $^{14}\text{C}$ -parathion residues in flooded soils over one month was associated with a near proportional increase of unextractable residues; aminoparathion, which resulted from the reduction of parathion, was absorbed about thirty times more than parathion itself.

### 5.5.2. *Volatilization*

Volatilization is the process by which applied pesticides are turned into vapor phase and subsequently lost into the atmosphere. Volatilization increases with increased pesticide concentration. The process is most active when the pesticide is applied on the surface of water or on wet soil, and at the beginning of the crop cycle when the rice canopy is not closed and the land is largely exposed. Incorporation of the pesticide immediately after application, even to a shallow depth, or application on dry soil will reduce volatilization losses.

Volatilization is a major cause of pesticide loss from target areas, particularly when they are applied to the surfaces of soils or plants. Volatilization loss often

exceeds that by chemical degradation. The effective life of pesticides in many instances may be limited by the rapid disappearance from the target area by volatilization and other means, resulting in the need for repeated applications, particularly in moist warm conditions of the tropics (Taylor and Spencer, 1990).

Soderquist, Bowers, and Crosby (1977) analyzed molinate and its degradation products at sub-ppm levels in water, soil, and air samples collected from a commercially treated field and showed that volatilization of molinate from water was the primary mode of dissipation, although photodecomposition products were present in field water. Substantial volatilization loss was also reported for HCH tested in the laboratory: 67 percent of  $^{14}\text{C}$ -gamma HCH was lost when applied to rice field water alone, 43 to 68 percent when applied to submerged soils, and 12 percent when applied to nonsubmerged soil (Siddaramappa and Sethunathan, 1976). Field measurements by Seiber, McChesney, Sanders, and Woodrow (1986) showed that volatilization was highest on the day of application and decreased rapidly. Volatilization rates varied within large limits depending on the nature of the pesticide. They reported values in  $\text{ng}/\text{cm}^2/\text{ha}$  on the day of application at 1.3 for 4-Chloro-o-cresol, 4.4 for MCPA, 37 for thiobencarb, and 575 for molinate.

Gaseous exchanges that take place between the soil and the atmosphere through the rice may favor losses of pesticides by volatilization, as observed for carbofuran. Siddaramappa and Watanabe (1979) observed by radiography a fairly rapid translocation of carbofuran, in significant amounts, to the foliage of rice seedlings after its application to flooded soil.

### 5.5.3. Diffusion

Diffusion is the process of fluid flow due to concentration gradient. Diffusion takes place in both gaseous and liquid phases of pesticides applied on ricefields. The process is governed by Fick's law, which states that the rate of diffusion in a given direction is proportional to the concentration gradient in that direction. Decreasing bulk density or increasing temperatures raises coefficient (Ehlers, Farmer, Spencer, and Letey 1969). Pesticides applied on ricefields are in a state of continuous flux due to the diffusion process, even if not by other forces, in nature's equilibrium-seeking behavior. Diffusion may control volatilization of pesticides.

When a pesticide is applied on dry soil or plant canopy, its volatilization will depend on the upward diffusion to the open surface as a concentration gradient is established (Taylor and Spencer, 1990). When a pesticide is incorporated into the soil by cultivation, the rate at which it volatilizes is controlled by its movement through the body of the soil to the overlying air. Because the diffusion path length to the surface is longer for incorporated pesticide, compared to the

condition when the chemical is applied on the top of the soil, volatilization of incorporated pesticide will be greatly restricted.

In an experiment where [ $^{14}\text{C}$ ]phorate was mixed with soils prior to soil submersion, residues were readily released from submerged soils into water, amounting to 45 percent of applied radiocarbon during the first three days after flooding. After a two-week incubation period as much as one-half of the radiocarbon applied to the soil was recovered from the water. Phorate was the principal compound recovered from submerged soils where it accounted for approximately 70 percent of the total residues recovered. Phorate sulfoxide was the major metabolite present in the water (Walter-Echols and Lichtenstein, 1978).

#### 5.5.4. *Percolation*

Percolation is the vertical downward movement of water due to gravitational force. With percolating water, pesticides dissolved in water or absorbed by particulate matters in the water move from the point of application to a deeper horizon of the soil profile. Through this process the chemicals can reach the water table and then move with the water table. Water-soluble formulations move faster in soil than the oil-soluble formulations. Adsorption of pesticides by soil reduces the effective movement of pesticides in the soil profile, which occurs significantly in soil that is rich in organic matter. That is why pesticides applied on ricefields may take a long time, even years, before they can be traced in deeper layers of the soil.

Pesticides would leach more readily in sandy soils than in clay soils because in sandy soils adsorption of pesticides is less and percolation rate higher. Puddling in lowland ricefields retards the transport of pesticides to the subsoil because it creates a less permeable soil in the plowed zone. Ramanand, Sharmila, and Sethunathan (1988) recovered a substantial amount of carbofuran from the leachates of unpuddled ricefields at both the 15 cm and 30 cm soil depths, but in puddled soil the mobility of carbofuran was found limited up to 15 cm and almost negligible at the 30 cm depth. Most pesticides would probably persist in the subsoil, but their accumulation would be a potential source of groundwater contamination in the long run. Some authors have however assumed that pesticides would not leach to groundwater except under rare circumstances (Hallberg, 1987).

#### 5.5.5. *Runoff*

Runoff, the lateral movement of water on land surface, may be responsible for pesticide transport away from the target area. Runoff results from excessive application of irrigation water or rainfall or from draining of the field to get rid of the water. Pesticides in runoff water from ricefields may be both in suspension

and adsorbed in colloidal particles. The time interval between the application of the pesticides and the rainfall or applied irrigation sufficient to produce runoff has significant effect on the amount of pesticide transported by runoff. Rainfall would wash off pesticide sticking to canopy and other parts of the plant body and move it to the standing water or soil surface, from where it may be transported by runoff.

Runoff water from ricefields is ultimately discharged into large bodies of water such as lake, rivers, or sea. Therefore, the contamination of freshwater bodies from pesticides transported by runoff is a matter of concern. Many previous studies have documented the serious effects of toxicity developed from agricultural pesticides on aquatic life, especially fish (see Chapter 8).

Very few studies have been conducted to quantify pesticide losses through runoff from ricefields. At the IRRI experimental farm organophosphates and carbamates in runoff water were found to be on the average at 1.0 ppb, with a range of 0 to 20.0 ppb (IRRI, 1988), which are considered low. Several studies in the United States showed that pesticide losses through runoff from field crops are small. Wauchope (1978) reported that for the majority of commercial pesticides total losses of pesticides in runoff water are 0.5 percent or less of the amount applied, unless severe rainfall occurred within one to two weeks after application. Willis, Rogers, and Southwick (1975) reported that the highest concentration of runoff loss over a three-year period of the applied diuron, linuron, fenac, and trifluralin were 0.12 percent, 0.30 percent, 2.90 percent, and 0.05 percent, respectively. These values were present in runoff water associated with rainstorms that occurred soon after application.

### *5.5.6. Absorption by Crop or Animals*

Pesticides applied to protect a crop can be absorbed by the crop itself, which is subsequently removed from the field on harvest, and thus they can enter the food chain. Ricefield-residing flora and fauna can also absorb the chemicals and contribute to through natural movements or harvest. These aspects are covered in the next section.

## **5.6. Persistence and Partition in the Ricefield Ecosystem**

### *5.6.1. Persistence*

The term persistence is used to express both the duration of the chemical's efficacy and undesirability; i.e., persistence for less than the desired time may

result in poor efficiency, while persistence beyond this time may lead to residue problems (Saltzman and Yaron, 1986). "Persistence time" is the time required for pesticide concentration to decline to 10 percent of the initial value. "Half-life" describes the dissipation rates, which is about 0.3 of the persistence time (Wauchope, 1978). Table 5.2 summarizes the half-life of pesticides in rice soils under different conditions. The half-life is often shorter under flooded conditions; soil sterilization often markedly increases half-life, showing the relative importance of microbial decomposition of pesticides.

### 5.6.2. *Partition in the Components of the Ricefield Ecosystem*

The relative extents of pesticide partition in the components of the ecosystems—in air, water, soil, and vegetation—vary with the mode of application and the nature of the pesticides, but soil and water invariably account for most of the pesticide in ricefields. Ross and Sava (1986) followed the fate of two herbicides, granular thiobencarb and molinate, broadcast in ricefields for thirty-two days after application. Maximum thiobencarb concentrations in air, water, soil, and vegetation were 1.4  $\mu\text{g}/\text{m}^3$ , 576  $\mu\text{g}/\text{L}$ , 3860  $\mu\text{g}/\text{kg}$ , and 1750  $\mu\text{g}/\text{kg}$ , respectively. The mass balance budget indicated that thiobencarb was predominantly distributed between water (34 percent) and soil (43 percent), and only less than 1 percent was located in air and vegetation. Maximum molinate concentrations in air, water, soil, and vegetation were 48  $\mu\text{g}/\text{m}^3$ , 3430  $\mu\text{g}/\text{L}$ , 2210  $\mu\text{g}/\text{kg}$ , and 918  $\mu\text{g}/\text{kg}$ , respectively. The mass balance budget indicated that as much as 81 percent of the molinate applied was dissolved in water followed by soil (10 percent), air (9 percent), and vegetation (less than 1 percent). Partitioning of these herbicides in the field was closely related to their physicochemical properties.

Isensee, Kaufman, and Jones (1982) used a rice microcosm to study the fate of 3,4-dichloroaniline (DCA), a major metabolite of the herbicide propanil (3',4'-dichloropropionanilide), in ricefields. Soil treated with 10 ppm DCA was placed in glass chamber, planted to rice, and flooded when the rice reached the two-leaf stage. After flooding, four species of aquatic organisms (algae, snail, daphnid, fish) were added. The concentration of DCA and metabolites in soil, rice, water, and aquatic organisms was determined over time. A maximum of 2.8 percent of the total radioactivity applied to soil desorbed or leached into water. DCA recovered from water decreased from 12 to 1 percent of the total radioactivity in water between one and thirty days after flooding. Between 10.5 and 18.5 percent of the radioactivity remaining in soil at the end of the experiments was extractable. Of the radioactivity recovered, between 5 and 11 percent was DCA, and up to 6 to 19 percent was 3,3', 4,4'-tetrachloroazobenzene (TCAB), the percentages

Table 5.2. Half-Life (Days) of Pesticides Tested in Wetland Rice Soils

<i>Pesticide</i>	<i>Half-Life (Days)</i>	<i>References</i>
2,4,5,-T	17-45	— Yoshida, 1975
2,4-D	28-36	— Yoshida, 1975
Alpha BHC	22-42	— MacRae, Raghu, and Castro, 1967; Ferreira and Raghu, 1981
Amiprophos	10	— Tomizawa, 1975
Basagran	3	— Higashi and Crosby, 1987
Benefin	4	— Probst and Tepe, 1969
Bentazon	3	— Higashi and Crosby, 1987
Benthiocarb	> 80	— Nakamura, Ishikawa, and Kuwatsuka, 1977
Beta BHC	22-65	— MacRae, Raghu and Castro, 1967; Ferreira and Raghu, 1981
BHC	20	— Yoshida and Castro, 1970
Buprofezin	104	— Funayama, Uchida, Kanno, and Tsuchiya, 1986
Butachlor	1-12	— Chen, 1980
Carbaryl	14-49	— Gill and Yeoh, 1980; Sethunathan, 1984
Carbofuran	19-70	— Siddaramappa, Tirol, and Watanabe, 1979; Venkateswarlu, Gowda, and Sethunathan, 1977
Chlomethoxynil	15	— Matsunaka and Kuwatsuka, 1975
Chlordane	> 90	— Castro and Yoshida, 1971
CNP	15	— Matsunaka and Kuwatsuka, 1975
DCNA	5-30	— Wang and Broadbent, 1973
DDT	> 45	— Castro and Yoshida, 1971
Delta BHC	32-50	— MacRae, Raghu, and Castro, 1967; Ferreira and Raghu, 1981
Diazinon	13-15	— Sethunathan and MacRae, 1969; — Sethunathan and Siddaramappa, 1978
Disulfoton	25	— Agnihotri, 1978
Endrin	7-55	— Gowda and Sethunathan, 1976
Gamma BHC	12-40	— MacRae, Raghu, and Castro, 1967; Raghu and MacRae, 1966 — Ferreira and Raghu, 1981
Heptachlor	75-90	— Castro and Yoshida, 1971
Hinosan	4	— Rajaram and Sethunathan, 1976
Isoxathion	< 20	— Nakagawa, Ando, and Obata, 1975
Kitazin	14	— Tomizawa, Uesugi, Ueyama, and Yamamoto, 1976
Metoxychlor	> 90	— Castro and Yoshida, 1971
Metoxychlor	90	— Castro and Yoshida, 1971
Molinate	2-96	— Deuel, Turner, Brown, and Price, 1978; Higashi and Crosby, 1987
Nitrofen	11	— Matsunaka and Kuwatsuka, 1975
Ordram	6	— Higashi and Crosby, 1987
Parathion	4-23	— Reddy and Sethunathan, 1983; Sethunathan, 1973b; — Sethunathan and Yoshida, 1973c
PCNB	20	— Wang and Broadbent, 1973
PCP	30	— Matsunaka and Kuwatsuka, 1975
Phorate	20	— Agnihotri, 1978
Picloram	60	— Yoshida, 1975
Propanil	1	— Matsunaka and Kuwatsuka, 1975
Pyrazoxyfen	4-34	— Arita and Kuwatsuka, 1991
Sevin	13	— Sethunathan and Siddaramappa, 1978
Swep	2	— Matsunaka and Kuwatsuka, 1975
Trifluralin	10	— Probst et al., 1967

being dependent on exposure time. Rice accumulated 0.5 percent or less of the total radioactivity in soil. Only 35 to 55 percent of the accumulated radioactivity was extractable. Very small amounts of radioactivity were accumulated by aquatic organisms.

Kearney, Smith, Plimmer, and Guardia (1970) determined propanil and propanil residue (3,3', 4,4'-tetrachloroazobenzene: TCAB) in rice soils with known histories of propanil application. Concentration of propanil and occurrence of TCAB decreased with increasing time and depth in soil. For total propanil applications ranging from 7 to 13.5 kg/ha, concentrations of propanil in the upper 10 cm of soil were around 0.1 to 0.2 ppm two to six weeks after the last application and lower than 0.02 ppm one year after application. Concentrations of TCAB were between 0.16 and 0.01 ppm two and six weeks after the last application and lower than 0.02 ppm one year after application.

A study of the fate of phorate in a soil-water-plant system using *Elodea* as plant component showed that fourteen days after application and thorough mixing with soil, soil, water, and plants contained 32, 39, and 17 percent of the applied radiocarbon, respectively (Walter-Echols and Lichtenstein, 1978).

In a microcosm study of the fate of  $^{14}\text{C}$ -lindane on rice-fish agricultural system, the distribution of  $^{14}\text{C}$  residues among the constituents of the model ecosystem was studied for ninety days (Mostafa, El-Arab, and Zayed, 1987). Lindane accumulated in fish and rice plant to a considerable extent. The insecticide was found to be readily absorbed by the roots and translocated to all parts of the rice plant. The peak level in the shoots (26 ppm) and roots (105 ppm) of plants was reached within three weeks. Concentration in the soil decreased from 1.8 ppm at seven days to 0.7 ppm at ninety days. Concentration in the fish reached a maximum after thirty days (90 ppm) and decreased to 40 ppm at ninety days. The data also showed a relatively low biodegradability of lindane in fish and rice plants.

### 5.6.3. *Absorption by Rice*

Pesticides in the food chain is a matter of serious concern. However, pesticide concentrations in rice grains have not been reported to reach a serious level from normal applications of pesticides. Tejada and Magallona (1986) found that of the seven pesticide formulations used, carbofuran and chlorpyrifos residues translocated to rice harvest but in levels that have no toxicological significance.

Rice seed, plant, and soil samples from the provinces of Iloilo, Bulacan, Nueva Ecija, the Mountain Province, and Palawan in the Philippines were analyzed for the presence of the four BHC isomers and DDT. Low levels of the four BHC isomers were detected in all the samples. The plants generally had a

higher BHC content than the soil. The amounts of BHC found in the grain and hull of rice were below the tolerance limit set by the United States Food and Drug Administration. DDT and its metabolites were identified in Palawan and the Mountain Province. The presence of DDT in the samples could have been due to the contamination from the DDT sprayed for malaria control in the dwelling places where the rice was stored (Del Rosario and Yoshida, 1976).

Seiber et al. (1978) found that residues of carbofuran or its carbamate metabolites in rice plants, from fields treated by soil incorporation or root-zone placement, did not exceed the 0.2 ppm tolerance allowed in whole grains by the United States Environmental Protection Agency standards. Residues above 0.2 ppm were found only in whole grains from plants that received six broadcast application of carbofuran at fourteen-day intervals throughout the growing season. Combined residues of carbofuran and 3-hydroxycarbofuran were less than 0.2 ppm in the grain from rice treated four times at twenty-day intervals. Thus, carbofuran underwent appreciable translocation to rice grain only after frequent or high-dosage applications that continued well into the second half of the growing season (Seiber et al., 1978).

Lee and Ong (1983) reported significant levels of lindane in rice grains collected from warehouse and milling plants. Up to 80 percent of the residues could be removed by repeated washing with water, a practice used before rice is cooked. Boiling further broke down the residues. Lindane was present in only trace amounts in farmers' rice although the chemical had been used in ricefields to control insect pests.

#### 5.6.4. Absorption by Plants and Animals

In some parts of Asia a wide range of edible plants and animals, including fish, are collected from ricefields for human consumption (Heckman, 1979).

Whereas bioconcentration of pesticides in the various elements of the food chain is a major topic of interest in pesticide studies, little attention has been paid to this aspect in ricefield studies. The few available data refer to pesticide accumulation *in vitro* by cyanobacteria common in ricefields (Das and Singh, 1977; Kar and Singh, 1979). However data from freshwater environments have demonstrated the ability of microalgae to accumulate pesticides (Wright, 1978). The consequences of this bioconcentration could be particularly important in integrated rice-aquaculture systems.

Tejada and Magallona (1986) also found that aquatic plant "kangkong" (*Ipomoea aquatica*), when grown in water containing 0.13 mg/liter of carbofuran, rapidly absorbed carbofuran. This is typical of systemic insecticides broadcast into floodwater as granules which would penetrate the root zone and be subsequently

taken in by plants. Pesticide residues in “kangkong” were within acceptable daily intake level set for carbofuran by FAO/WHO (1977). The authors also showed that when carbofuran-contaminated rice leaves were fed to lactating goats for seven consecutive days, 77 percent of the dose was rapidly excreted in urine and very little was eliminated in feces (1 percent) and milk (0.5 percent). Residues were found in different tissues of goats but they were mostly nontoxic metabolites.

Certain aquatic animals have been reported to retain (bioaccumulate) pesticides in concentrations many times more than the concentrations in water. Bioaccumulation as a process is of concern in relation to pesticide toxicity in aquatic food. In their study of the fate of selected pesticides in rice-fish and livestock farming, Tejada and Magallona (1986) found carbofuran residues in fish at harvest, concentrated most in entrails, then in fillet and least in head; but the concentrations were below the maximum acceptable limit set for meat (0.05 mg/kg). Similar findings were reported by Argente, Seiber, and Magallona (1977) for carbofuran and Zulkifli, Tejada, and Magallona (1983) for chlorpyrifos.

A pesticide residue trial in a small scale rice-fish culture showed that fish and snails were able to accumulate carbofuran residues respectively 100 and 10 times more than the concentrations of residues in the water (Tejada and Magallona, 1986).

## 5.7. Environmental Contamination

Pesticides may be introduced directly into the environment in a liquid phase, as a dispersion or solution, or in the solid phase—as a powder, microcapsule, or granule. Sprays are directed to the foliage or the soil. Solids are applied directly to the soil surface or to foliage. Pesticides may be incorporated directly into the soil, usually at the top few millimeters to exert a biological effect. Pesticides may also enter the environment through accidental spill or waste disposal (Himel, Loates, and Bailey, 1990).

Environmental entry and transport processes start immediately after the pesticide has been applied. Irrigation or rainfall may modify the relative importance of the various components of these processes in determining the fate of the applied pesticide. Environmental sinks for pesticides include chemical, photochemical, and biological transformation, volatilization losses, erosion and runoff, leaching, and harvest removal and storage (Himel, Loates, and Bailey, 1990).

Figure 5.4 depicts the pesticide transport and transformation processes in the plant-soil-water environment.

The environmental pollution from pesticides is caused mainly by the physical processes of pesticide transfer. Several of these processes may be active

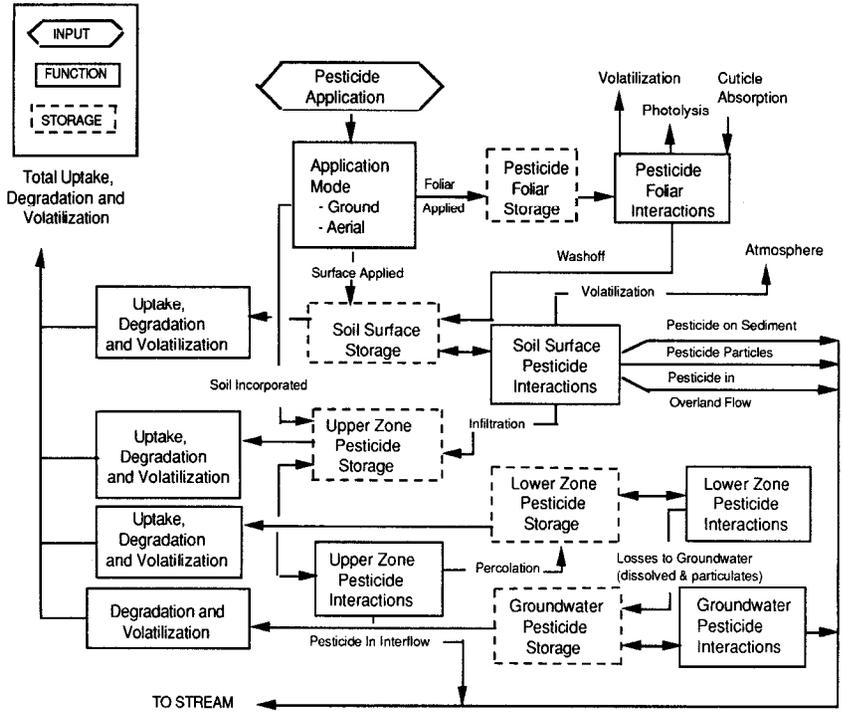


Figure 5.4. Pesticide Transport and Transformation in the Soil-Plant Environment and Vadose Zone

Source: After Donnigan and Crawford (1976).

simultaneously. Soil is contaminated by pesticide adsorption, surface water is contaminated by pesticides moved through runoff, groundwater quality is deteriorated by pesticides reaching the water table through leaching and deep percolation, and the atmosphere is polluted by the volatilization of pesticides. Through absorption by crops or aquatic animals, pesticide residues can get into human beings and animals that depend on them for food. Pesticide degradation processes decrease the severity of its concentrations in soil and water systems.

5.7.1. Surface Water Bodies

Runoff is the principal route for pesticides from ricefields to rivers, lakes, and marine ecosystems. Accumulation of pesticides in surface water bodies can have

far-reaching consequences for domestic water supply and aquatic organisms. Pesticide contamination of surface water bodies can be assessed by monitoring residue levels in aquatic food webs.

Herbicides used in ricefields have caused water quality problems in the Sacramento River, California, and restrictions have been imposed on their use to prevent or reduce contamination. The problem herbicides are thiobencarb, which gives a bitter taste to water, and molinate, which is toxic to fish. California regulations now require that, after the application of thiobencarb and molinate, water must be retained on the farm for fourteen and twelve days, respectively, to keep the concentration of thiobencarb in the river below 8 ppb and that of molinate below 4.5 ppb (Moody, 1990).

Aldrin applied to seed rice enters the aquatic ecosystem through ricefields and marshland drainage. Residue analysis of representative species of the aquatic biota indicated significant biological accumulation; rapid rise in the concentration of pesticides in living organisms resulted in a massive kill of aquatic organisms (Ginn and Fisher, 1974).

Herbicides applied in water reservoirs may have detrimental effects on rice. In southeastern Australia, acrolein, Dalapon, and TCA are applied in irrigation canals to control aquatic weeds. Bowmer et al. (1988) reported that seeded rice was damaged when exposed to acrolein-treated water. However, the rice was able to compensate for the early damage by tillering profusely and yields were increased by treatment with acrolein. To avoid detrimental effects of Dalapon or TCA on rice the time between treatment and water resupply to ricefields should be greater than six weeks (Bowmer, 1988).

We know very little about the problems of the kind discussed above about freshwater bodies of the third world countries, where pesticide use is increasing. A case study conducted in the Philippines is reported in Chapter 7.

### 5.7.2. *Groundwater System*

Groundwater contamination by agricultural chemicals is a major environmental pollution issue. In recent years, a number of organic contaminants have been detected in groundwater samples. In the United States, seventeen different pesticides have been detected in groundwater in twenty-three different states; the concentrations typically ranged from trace amounts to several hundred parts per billion (Sun, 1986). However, no systematic studies have been conducted for detection of groundwater contamination in rice-growing areas of Asia, where multiple rice cropping with associated intensive pesticide use has been commonly practiced for many years. Groundwater contamination is probably higher in such areas than in more traditional one crop per year areas, particularly when

the water table is shallow and the aquifer is overlain by light-textured soils (Castañeda and Bhuiyan, 1990).

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