Degradation of Organochlorine Insecticides in Flooded Soils in the Philippines

Teresita F. Castro and Tomio Yoshida*

The degradation of the organochlorine insecticides DDT, DDD, methoxychlor, heptachlor, chlordane, endrin, dieldrin, and aldrin was investigated under upland and flooded conditions. DDT, DDD, methoxychlor, and heptachlor degraded faster in flooded soil than in upland soil and were found to degrade faster in soils with high organic matter content. DDD was found to accumulate in DDT-treated flooded soil. Endrin was degraded only in Casiguran flooded soil. Aldrin was more persistent in flooded than in upland soil. Chlordane and dieldrin were persistent both in flooded and in upland soil.

Organochlorine insecticides such as DDT [1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane], DDD [1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane], methoxychlor [1,1,1-trichloro-2,2-bis(*p*-methoxyphenyl)ethane], heptachlor [1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene], chlordane [1,2,4,5,6,7,8,8-octachloro-3a,4,-7,7a-tetrahydro-4,7-methanoindan], endrin [1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-*endo*-1,4-*endo*-5,8-dimethanonaphthalene], dieldrin [1,2,3,4,10,10-hexachloro-*exo*-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo*,*exo*-5,8-dimethanonaphthalene], and aldrin [1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-*endo*-1,4-*exo*-5,8-dimethanonaphthalene] have been extensively used for the last 25 years. These insecticides are considered to be persistent chemicals in the natural environment. Recently the use of insecticides has been limited in many countries because of the undesirable residues of such chemicals in foodstuffs and their interference with the natural reproductive cycle of some mammalian species.

Alexander (1965) suggested that, at least in the soil, these pesticides are either nonbiodegradable or are detoxified so slowly that they can be considered effectively nonbiodegradable. In flooded soil, however, a chlorinated hydrocarbon insecticide, γ-BHC, has been found to degrade with less residue problems (MacRae *et al.*, 1967; Yoshida and Castro, 1970) and also a bacterium isolated from the soil has been found that degrades the chemical under anaerobic conditions (Sethunathan *et al.*, 1969). DDT also is degraded to a great extent in an anaerobic environment such as flooded soil (Guenzi and Beard, 1968; Ko and Lockwood, 1968), waste water sludge (Hill and McCarty, 1967), and lake impoundments (Newland *et al.*, 1969).

This paper presents the results of studies on the organochlorine insecticides DDT, DDD, heptachlor, methoxychlor, chlordane, endrin, dieldrin, and aldrin in four Philippine soils.

MATERIALS AND METHODS

Soil Preparation. The soils used were Maahas clay (pH 6.6, organic matter: 2.0%; total nitrogen: 0.14%), Luisiana clay (pH 4.7, organic matter: 3.2%; total nitrogen: 0.21%), Pila clay loam (pH 7.6, organic matter: 1.5%; total nitrogen: 0.09%), and Casiguran sandy loam (pH 4.8, organic matter: 4.4%, total nitrogen: 0.2%). The soil samples were prepared by essentially the same procedure as reported previously by Yoshida and Castro (1970). The soils were air-dried, passed through a 2-mm sieve, and 20-g samples were placed in test tubes (25 × 180 mm). The experiment was conducted under upland and submerged conditions. In the upland condition, water was provided to give 80% of the maximum water-holding capacity of each soil. This level was maintained by adding twice a week the amount of water that was lost due to evaporation. The submerged condition was maintained at a water level of 5 cm above the soil surface. All treatments were duplicated.

The following insecticides were used: DDT (99%), DDD (100%), methoxychlor (89.5%), heptachlor (74%), chlordane (100%), endrin (99%), dieldrin (100%), and aldrin (90%). These chemicals were purchased from the Polyscience Corp., Evanston, Ill. Stock solutions of each insecticide were prepared by dissolving the chemicals in redistilled hexane. About 15 ppm of the insecticides from a stock solution was added to the soil. The solvent, hexane, was evaporated by passing a stream of air over the mixture of the stock solution and soil for 6 hr in an incubation chamber at 30° C before adding the flood water. The soils were thoroughly mixed with the chemical before the water was added. The samples were placed in an incubation chamber at 30° C. Soils without added chemicals served as controls. Each organochlorine insecticide in each soil sample was extracted and analyzed by gas chromatography. The samples were analyzed for DDT every 15 days for 45 days and for DDD after 1, 2, and 6 months. The samples were analyzed for heptachlor at 15 days and then every month after the beginning of the incubation period. Amount of methoxychlor in the samples was analyzed every month except in the Casiguran flooded soil from which, during the first month, samples were analyzed every 10 days. The samples were analyzed for chlordane, endrin, dieldrin, and aldrin every month. The samples were incubated for 3 months except those containing DDT and DDD. The extraction procedure of Yoshida and Castro (1970) was used.

Gas Chromatography. A Perkin-Elmer vapor fractometer, Model 154D, with an electron capture detector was used to analyze for DDT, DDD, and aldrin. A U-shaped glass column (3-ft long and 0.25-in. in outer diameter) was packed with 4% SE-30 (methyl) and 6% QF-1 in acid-washed Chrom W. The operating temperature was 180° C and the attenuation used was 32. The amounts of methoxychlor, heptachlor, chlordane, endrin, and dieldrin were measured with a Varian Aerograph Model Series 1700 (Wilkens Instrument and Research, Inc., Walnut Creek, Calif.) fitted with dual columns and electron capture detector. The gas chromatographic method of Burke and Holswade (1966) was used with some modifications. The spiral glass columns were 6-ft × 1/8-in. (outer diameter) packed with equal portions of 15% QF-1 on 100/120 Gas Chrom Q and 10% DC 200 on 100/120 Gas

Department of Soil Microbiology, The International Rice Research Institute, Los Baños, Laguna, Philippines.

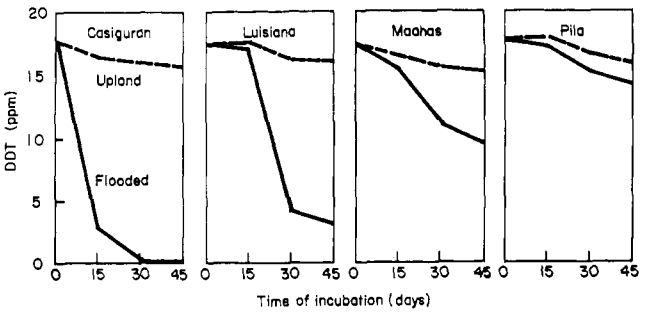

Figure 1. Degradation of DDT in four soils

Chrom Q. The column temperature was 200° C; the injection temperature was 225° C; and the detector temperature was 180° C. The carrier gas was a prepurified nitrogen (Matheson Co., Inc.) maintained at the flow rate of 12 ml/min. Standard curves for each insecticide were made for every analysis.

RESULTS

The residue curve of DDT during the incubation (Figure 1) resembled that of lindane in flooded rice soil, as previously reported by Yoshida and Castro (1970). DDT was degraded the fastest in the Casiguran soil and the slowest in the Pila soil. In the soil with the highest organic matter content (Casiguran), DDT was degraded much more rapidly under the flooded soil conditions than under upland conditions. Only small losses of DDT occurred under upland conditions in all four soils. DDD, a possible first intermediate of DDT, was detected in the gas chromatograms in the flooded conditions within the first 30 days of incubation. The largest amount of DDD accumulated in the Casiguran soil. After 30 days 13.0 ppm of DDD was found in Casiguran soil, 5.8 ppm was found in Luisiana soil, 4.7 ppm was found in Pila soil, and a trace amount was found in Maahas soil. No intermediate other than DDD was found in the gas chromatograms. DDT was not converted to DDD in the upland soil. When DDD was added to the soils, it was more persistent than DDT, but the amount of both DDT and DDD residues in flooded Casiguran or Luisiana soil was very small after 6 months (Figure 2).

Methoxychlor seemed to degrade about as fast as DDT (Figure 3). But the loss of the insecticide in upland soils during 3 months of incubation was relatively high. Heptachlor also had much less residue under flooded conditions than under upland conditions (Figure 4). Heptachlor showed almost the same pattern of degradation as did methoxychlor. A relatively high loss of methoxychlor and heptachlor was found under upland conditions as compared to DDT. There is considerable evidence indicating that the organochlorine

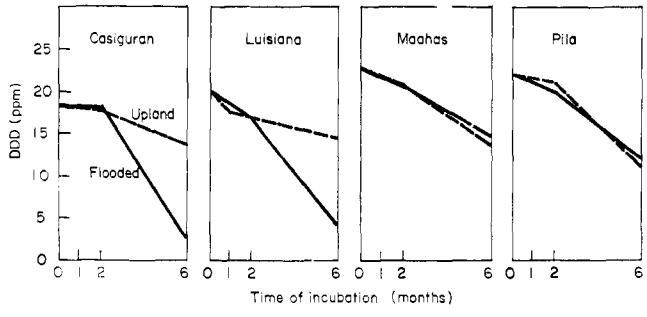

Figure 2. Degradation of DDD in four soils

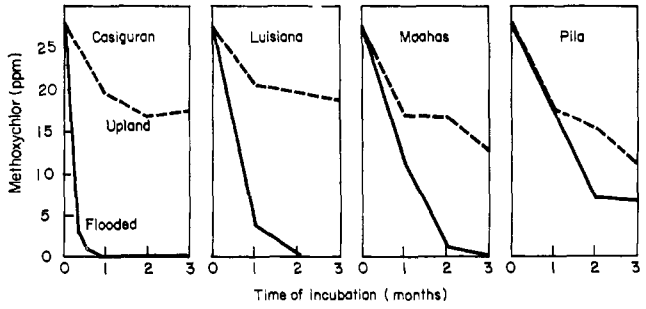

Figure 3. Degradation of methoxychlor in four soils

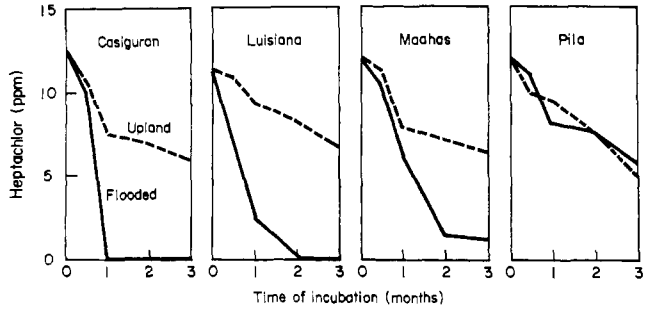

Figure 4. Degradation of heptachlor in four soils

insecticides are volatilized in soil (Edwards, 1966). Some of the losses of DDT, DDD, methoxychlor, and heptachlor under upland condition were probably caused by chemical volatilization and adsorption by the soil colloids or organic matter. Our recent results (Castro and Yoshida, 1970) showed that the disappearance of heptachlor and DDT in sterilized Casiguran flooded soil was very much slower than in the nonsterilized Casiguran flooded soil, indicating the biodegradation rather than chemical degradation of the insecticides.

Chlordane and dieldrin remained quite stable for 3 months in all soils (Figures 5, 6). Endrin was unstable only in the

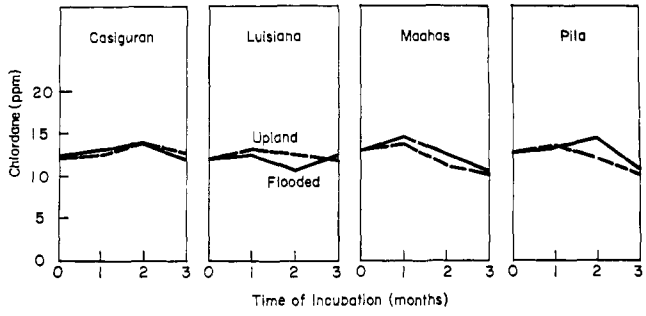

Figure 5. Degradation of chlordane in four soils

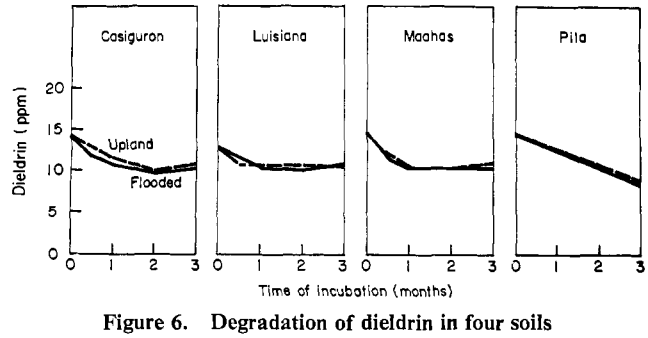

Figure 6. Degradation of dieldrin in four soils

flooded Casiguran soil; after 2 months only 8.4% of the chemical was recovered in the flooded soil, while 88.24% was recovered in the upland soil. In all other soils, endrin persisted for 2 months. The flooded soils had larger amounts of residues of aldrin than the upland soils. Under upland conditions, after 2 months' incubation, 44% of added aldrin remained in the Pila soil, 46% remained in the Maahas soil, 58% remained in the Luisiana soil, and 33% remained in the Casiguran soil. Under flooded conditions 65% remained in the Pila soil, 81% remained in the Maahas soil, 74% remained in the Luisiana soil, and 64% remained in the Casiguran soil.

DISCUSSION

Most organochlorine insecticides are considered to be persistent chemicals in the natural environment. We found, however, that DDT, DDD, methoxychlor, and heptachlor degrade readily in flooded soils. Although other workers have considered that losses of these insecticides are largely due to volatilization, our studies with sterilized and nonsterilized soils show that volatilization losses are minor compared to those resulting from microbial degradation (IRRI Annual Report, 1970). Sethunathan *et al.* (1969) showed that the γ-BHC bacteria which degrade lindane also degrade DDT, suggesting the occurrence of a common biochemical function called "reductive dechlorination," where one chlorine atom is replaced by one hydrogen atom. In the flooded soils, DDT was degraded to DDD. Chacko *et al.* (1966), Guenzi and Beard (1968), and Sethunathan *et al.* (1969) identified DDD as an intermediate of DDT under anaerobic conditions and showed that it accumulated in the soil. After 6 months DDD, however, was more rapidly degraded in flooded Casiguran and Luisiana than in the same soils under upland conditions. Ko and Lockwood (1968) found that DDD did not degrade in submerged soils when incubated with 1 to 5% chopped alfalfa for 5 weeks, although the DDT degradation was stimulated by the same treatment. They found that DDD had a broader antimicrobial spectrum and a greater toxicity to microorganisms than DDT. Methoxychlor and heptachlor degraded faster in flooded soils than did DDT. It is interesting that heptachlor, a cyclodiene insecticide, degraded, whereas chlordane, another cyclodiene possessing a very similar chemical structure, did not. Lichtenstein *et al.* (1970) showed that heptachlor undergoes epoxidation to yield heptachlor epoxide in soil. Under the flooded conditions, however, none of the soils showed the accumulation of heptachlor epoxide, the intermediate of epoxidation. Dieldrin was very persistent even in flooded soil. Except in Casiguran soil, endrin also was persistent in flooded soil. Chlordane and dieldrin are considered as nonbiodegradable insecticides under experimental conditions. Aldrin was more stable in flooded than in upland soil probably because molecular oxygen was inadequate for the epoxidation of the chemical. Aldrin undergoes epoxidation to yield dieldrin in soil (Lichtenstein *et al.*, 1970).

We found also that the rate of degradation of some organochlorine insecticide and the soil's organic content were correlated: the high content of organic matter in the soil favored the degradation. The organic matter accelerates the decline of the oxidation-reduction potential of the soil (Ponnamperuma, 1964) which should be more favorable for the microbial function in the "reductive dechlorination" (Plimmer *et al.*, 1968). Ko and Lockwood (1968) reported that the addition of 1% chopped alfalfa greatly enhanced the conversion of DDT to DDD in submerged soil but not in moist aerobic soil. We observed (Yoshida and Castro, 1970) that γ-BHC degradation was enhanced in flooded soils by the addition of rice straw but was depressed by the addition of oxidized compounds. Probably the facultatively anaerobic or anaerobic bacteria abundant in these soils become active in the reductive dechlorination only after the oxidation-reduction potential reached a certain value for the biochemical reaction. Higher organic matter content would provide a better environment for the anaerobic metabolism. It may also be possible that these microorganisms use these compounds as a hydrogen or electron acceptor in their microbial metabolism. The bacteria metabolizing more organic materials require more hydrogen acceptors in anaerobic conditions. Individual microflora may be able to reductively dechlorinate several organochlorine insecticides. For example, the isolate from the soil which degrades γ-BHC degrades the DDT to DDD (Sethunathan *et al.*, 1969) so it is highly possible that DDT, methoxychlor, and heptachlor can be used by a soil microflora as a common substrate for reductive dechlorination. On the other hand, some microflora may reductively dechlorinate only one specific organochlorine insecticide.

LITERATURE CITED

Alexander, M., *Soil Sci. Soc. Amer. Proc.* **29,** 1 (1965).
Burke, J. A., Holswade, W., *J. Ass. Offic. Anal. Chem.* **49,** 374 (1966).
Castro, T. F., Yoshida, T., unpublished data, 1970.
Chacko, C. I., Lockwood, J. L., Zabik, M., *Science* **154,** 893 (1966).
Edwards, C. A., *Residue Rev.* **13,** 83 (1966).
Guenzi, W. D., Beard, W. E., *Soil Sci. Soc. Amer. Proc.* **32,** 522 (1968).
Hill, D. W., McCarty, P. L., *J. Water Pollut. Contr. Fed.* **39,** 1259 (1967).
International Rice Research Institute, Annual Report 1970, Los Baños, Philippines, 1970.
Ko, W. H., Lockwood, J. L., *Can. J. Microbiol.* **14,** 1069 (1968).
Lichtenstein, E. P., Schultz, K. R., Fuhremann, T. W., Liang, T. T., J. Agr. Food Chem. **18,** 100 (1970).
MacRae, I. C., Raghu, K., Castro, T. F., J. Agr. Food Chem. **15,** 911 (1967).
Newland, L. W., Chester, G., Lee, G. B., *J. Water Pollut. Contr. Fed.* **41,** 174 (1969).
Plimmer, J. R., Kearney, P. C., Van Endt, D. W., J. Agr. Food Chem. **16,** 594 (1968).
Ponnamperuma, F. N., "The Mineral Nutrition of the Rice Plant," Maryland, 1964, p 295–328.
Sethunathan, N., Bautista, E. M., Yoshida, T., *Can. J. Microbiol.* **15,** 1349 (1969).
Yoshida, T., Castro, T. F., *Soil Sci. Soc., Amer. Proc.* **34,** 440 (1970).

Received for review February 5, 1971. Accepted April 29, 1971.