Decomposition of Pesticides by Soil Microorganisms
— Special Emphasis on the Flooded Soil Condition—

By IWAO WATANABE

Assistant Professor, Faculty of Agriculture, Iwate University

It is estimated that every year the foliage and soils of Japan are doused with approximately 80,000 ton of synthetic pesticides and it is claimed that an annual dose of pesticides per acre of Japanese arable land is the greatest in the world.

Recently, warning has been issued on the pollution and disturbance of ecosystems by pesticides which may cause a health hazard.

Most of the agricultural investigators have been relatively indifferent to the fate of pesticides in soils and other environments until a recent increase of the charge against environmental pollution.

The contamination of soil by synthetic pesticides and their degraded products may exert a pronounced effect on soil metabolism.

Soil may be considered as an excellent medium of the decontamination of synthetic organics due to its high power of absorption and its versatility of degrading ability.

Dense population of microorganisms in the soil is mainly responsible for the decomposition of pesticides. Nearly a half of the amount of pesticides consumed in Japan was applied to the paddy field.

Soil condition of the flooded rice field differs greatly from that of the upland soil. The persistence and metabolism of pesticides in the flooded paddy soil, therefore, may differ.

Information on the pesticides' persistence in upland field or soil has been given mostly by foreign investigators. Considering the fate of pesticides in the flooded rice soil of Japan, such information must be reexamined.

In this review, special emphasis is made on the difference of the pesticides' persistence and metabolism between the flooded soil and upland soil. Contributions to the pesticides' fate in the flooded soil have been made by the Japanese investigators and these are described hereunder.

Herbicides

PCP (pentachlorophenol): Until recently, PCP was the most widely used herbicide in Japan. Owing to its high toxicity to fishes, PCP has been, however, gradually replaced by the other herbicides. PCP is used before and after rice transplantation.

The herbicidal activity persists approximately for two or three weeks. Rapid loss of its phytocidal activity after its application on rice field is responsible partly for photodecomposition. KUWAHARA and others[1),2)] identified several decomposed products after sunlight irradiation, among which the presence of dioxane must be noted. It is not probable that PCP introduced into the soil layer is photochemically degraded.

WATANABE and HAYASHI[3)] suggested that PCP may be decomposed by the microbial action under the dark and flooded soil condition in the laboratory. Sterilization stopped PCP depletion.

Subsoil or newly reclaimed paddy soil poor in organic matter was less active in the depletion of PCP and the inoculation of the aged paddy soil accelerated the depletion. Successive addition of PCP after its disappearance hastened PCP depletion, suggesting the enrichment of responsible microorganisms.

Under the flooded condition employed (depth of the surface water layer is about 1 cm), the enriched PCP's depletion activity was shown to be of aerobic nature.

WATANABE[4] succeeded in isolating PCP decomposing *Pseudomonas* from the soil perfused with PCP solution. The isolates were capable of growing on PCP (40 ppm) as a carbon source and decomposing PCP to liberate five chlorine atoms. The bacteria were not active in decomposing PCP under anaerobic condition. The chemical nature of a metabolite remains to be elucidated.

KUWATSUKA[5),6)] compared the PCP decomposition rate between upland and flooded soil condition in the dark at the laboratory. After pre-incubation, PCP was added. In general, the PCP degradation rate was higher in the flooded soil than in the upland.

A half life of PCP at 100 ppm in arable land soil was 10 to 40 days at 30°C. Among soil properties, organic matter content was most closely related to the rate of PCP degradation. As degraded products, 2,3,4,5-,2,3,4,6-, and 2,3,5,6-tetrachlorophenols and 2,3,6-,2,4,6-2,3,5- and 2,3,4- and/or 2,4,5-trichlorophenols were detected by gas chromatography. At 10 ppm concentration, tetra and trichlorophenols were produced on the flooded and non-flooded conditions. KUWATSUKA suggested the degraded process was partly chemical and partly microbiological.

NIKI and others[7] also detected tetra and trichlorophenols in the PCP-treated flooded soil. SUZUKI and NOSE[8),9)] isolated the Gram positive rod shaped bacteria from the PCP-treated well drained soil. At 1 ppm concentration, PCP was shown to be converted to pentachloroanisol ($C_6Cl_5OCH_3$) by cell suspension.

Besides this, 2,3,5,6-tetrachlorohydroquinone dimethyl ether was formed via tetrahydroquinone. Methylation of PCP was also detected by CSERJESI and JOHNSON[10] using *Tricoderma*. In both cases, PCP concentration was less than 10 ppm.

Swep and Propanil: Swep (MCC, N-3, 4-dichlorophenylcarbamate) and Propanil (Stam, DCPA, 3,4-dichlorophenylpropioanilide) are related to each other by their structures. Swep is used mainly on soil surface treatment and Propanil is employed on foliar application to rice. Metabolism of phenylcarbamate herbicides is reviewed by HERRETT[11] and that of acylanilide herbicides by BARTHA and PRAMER[12].

In upland soil, it is reported that both compounds give dichloroaniline after hydrolysis. Coupling of dichloroaniline gives 3,4,3′,4′-tetrachloroazobenzene which can be detected in the soil in the course of Propanil degradation.

KUWATSUKA[5] investigated Swep and Propanil degradation in the flooded and non-flooded soil. He detected dichloroaniline and the coupled azobenzene in Swep or Propanil-treated soil on both conditions. At 30°C, Propanil was less persistent than Swep on both conditions. Soil flooding accelerated the degradation of Propanil and the reverse is the case in Swep.

Benthiocarb: Benthiocarb (Saturn, p-chlorobenzyl N, N-diethylthiocarbamate) was in practical use since 1970 and is now one of the popular herbicides for paddy fields. KUWATSUKA[5] studied the fate of Benthiocarb in flooded soil. A half life of this carbamate in flooded soil at 20 ppm at 30°C varied greatly according to the different conditions of soil, ranging from six to more than 40 days. The difference of the persistence between flooded and non-flooded soil was variable.

Diphenyl ethers: Various compounds of this series are now used as the soil surface treated-herbicides for rice culture. CNP (MO, 2,4,6-trichlorophenyl 4′-nitrophenyl ether) and nitrophen (Nip, 2,4-dichlorophenyl

4′-nitrophenyl ether) are widely used. The persistence of Nip on paddy field is short. ICHIHASHI et al.[13] studied the fate of diphenyl ether herbicides in soil and found the reduced amino derivatives in enriched soil solution with diphenyl ethers.

KUWATSUKA[5),14] studied the fate of three diphenyl ethers (Nip, 2,4-dichlorophenyl 3′-methoxy 4′-nitrophenyl ether and 2,4-dichloro 6-fluorophenyl 4′-nitrophenyl ether) in upland and flooded soil in the laboratory.

The degradation was much slower in upland than in flooded soil. In flooded soil, a half life of Nip was 10 days or so at 30°C Other ethers persisted longer. In the flooded soil, amino derivatives were formed. Information on the cleavage of ether bond is not yet available.

Insecticides

Organic chlorine insecticides: It is well known that organic chlorine insecticides are, in general, the most persistent among synthetic pesticides. Owing to the resistance to degradation, the contamination of environments by organic chlorine insecticides has been a serious problem.

Recently, most of the organic chlorine pesticides have been prohibited to use or permitted only for a limited purpose in Japan. BHC and DDT are reported to persist for several years in upland field. These are, however, greatly susceptible to degradation under the anaerobic condition.

CASTRO and YOSHIDA[15] reported that a half life of gamma BHC in flooded soil at 30°C was from two to four weeks. SETHUNATHAN and YOSHIDA[16] studied the degradation of gamma BHC by pure culture of *Clostridium* and showed that BHC was anaerobically dechlorinated. The same bacterium was capable of dechlorinating DDT anaerobically.

TATSUKAWA and others[17] reported that a residual amount of BHC in paddy field soil was not so large as expected from the large amount applied annually. (ca. 1000 g/ha).

This finding may be explained partly by the short persistence of BHC in the flooded soil. CASTRO and YOSHIDA[18] compared the persistence of several organic chlorine insecticides under the flooded and non-flooded soil condition in the laboratory at 30°C.

The results are summarized as follows.

(1) Degraded faster in flooded soil—BHC, DDT, DDD, methoxychlor and heptachlor.

(2) Degraded slower in flooded soil—aldrine.

(3) Persistent under both conditions—chlordane and dieldrin.

(4) Variable—endrin (degradable only in a case of flooded soil).

(5) Though DDD (dechlorinated product of DDT, still insecticidic) was degraded faster in the flooded soil, degration speed was much slower than that of DDT in flooded soil, resulting in the accumulation of DDT in flooded soil.

Organic phosphor insecticides: In place of parathione, highly toxic to human and organic chlorine insecticides, various kinds of organic phosphor insecticides have been used increasingly. In general, these organic phosphor insecticides are greatly susceptible to degradation. Among them, Diazinone (O,O-diethyl O-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate) persisted relatively long.

SETHUNATHAN and YOSHIDA[19] studied the fate of Diazinone in flooded soil. In such condition, Diazinone is rapidly hydrolyzed to yield 2-isopropyl-6-methyl-4-hydroxy pyrimidine which is resistant to further degradation under the flooded condition. Hydrolysis was suggested to be biological in some cases and chemical in acid soil. Responsible microorganisms were isolated.

YOSHIDA and SETHUNATHAN[20] isolated *Flavobacterium* capable of growing on Diazinone as a carbon source from the flooded water treated with Deazinone. The bacterium was capable of degrading it via hydrolysis and pyrimidine ring cleavage. Hydrolysis took place under aerobic and anaerobic conditions, but ring cleavage occurred only under the aerobic condition. This finding is compatible with the fate of Diazinone in soil.

The same bacterium had ability to hydrolyze parathione and Dursban but not malathone which has P-S-C bond. Major metabolite of parathione was p-nitrophenol. In flooded soil, reduced amino derivative of parathione was suggested to be formed.

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