

COMPREHENSIVE RESEARCH ON RICE

ANNUAL REPORT

January 1, 1977 - December 31, 1977

I. PROGRAM AREA AND TITLE: Rice Production-5; The Environmental Fate of Pesticides Important to Rice Culture.

II. PROJECT LEADERS AND PRINCIPAL UC INVESTIGATORS:

Project Leaders: D.G. Crosby, Professor; J.B. Bowers, Staff Research Associate IV. Principal Investigators: C.J. Soderquist, Staff Research Associate II; William Draper, Research Assistant.

III. LEVEL OF 1977 FUNDING: \$19,200.

IV. OBJECTIVES ACCORDING TO 1977 PROPOSALS AND EXPERIMENTS BY LOCATION CONDUCTED TO ACCOMPLISH THESE OBJECTIVES:

- A. Objective I. To investigate and identify environmental factors--especially oxidation and volatilization--which govern transport and chemical transformations of rice pesticides, with emphasis on molinate, benthocarb, Duter, and selected insecticides.
1. Molinate (Ordram): Construction of apparatus for studying effects of wind and temperature on evaporation of pesticides from water (UCD).
 2. Benthocarb (Bolero): Breakdown of p-chlorobenzyl sulfonic acid, a possible benthocarb terminal residue; effect of hydrogen peroxide and sunlight on benthocarb; detection of breakdown products in treated fields (UCD, Yuba and Sutter Co.s).
 3. Rice Field Reactants: Isolation and identification of hydrogen peroxide as the oxidant formed in water by the action of sunlight on organic compounds, study of reactions of hydrogen peroxide with rice pesticides, effect of sunlight on buildup of oxidants in water (UCD).
- B. Objective II. To examine the environmental distribution and dissipation of these chemicals under rice-field conditions.
1. Molinate: Laboratory studies with molinate in water to determine terminal residues; field studies of molinate vaporization; trapping of possible breakdown products in the air (UCD, Yolo Co.).
 2. Benthocarb: Analysis of soil samples from treated fields; laboratory verification of residues; identification of breakdown products in water from treated fields (UCD, Yuba and Sutter Co.).
 3. Duter: Study of hydrolysis rates, photolysis, and development of analytical methods for Duter and its breakdown products (UCD).

C. Objective III. To estimate the relative importance of each factor in the practical use of rice pesticides.

1. Duter: Hydrolysis and photolysis rates needed for registration (UCD).
2. Oxidants: A general mechanism of pesticide degradation in water; influence on residues and period of activity in controlling pests (UCD).
3. Volatility: The major pathway of dissipation of some rice pesticides (UCD).

IV. SUMMARY OF CURRENT YEARS WORK BY OBJECTIVE:

A. Objective I. Environmental factors which govern transport and transformation of rice pesticides.

An apparatus has been constructed to measure the effect of wind on evaporation of pesticides from water. This device maintains a constant level of water at a constant temperature in a stream of moving air. Airspeed may be varied from 2 to 5 mph and the rate of loss of pesticide from water to air determined. In our first series of tests with molinate the half life of dissolved molinate was 25 hours at all wind speeds with a water temperature of 26°C (79°F). Rate of water loss increased with increasing wind speed.

P-chlorobenzyl sulfonic acid (PCBSA) is a possible stable breakdown product of benthocarb. PCBSA does not absorb sunlight and did not breakdown in water when exposed to the sun. Addition of a sensitizer (acetone) caused some breakdown of PCBSA after 14 days. The breakdown products were p-chlorobenzaldehyde and p-chlorobenzoic acid - the same products obtained by benthocarb irradiation. Later work with hydrogen peroxide indicated that the sulfonic acid is probably not formed by photooxidation of benthocarb in rice fields.

An oxidant developed in both water containing tryptophan and in sterilized pond water when the solutions are exposed to sunlight. This oxidant was isolated and identified by various chemical and physical methods. It proved to be hydrogen peroxide. Sunlight irradiation of rice-field water produced oxidant which reached a concentration equivalent 9 micromolar hydrogen peroxide in 200 minutes. The concentration remained stable at this level in the light but when the water was placed in the dark the oxidant concentration dropped. Most of this light-generated oxidant had disappeared after 200 minutes of darkness (see Figure 1).

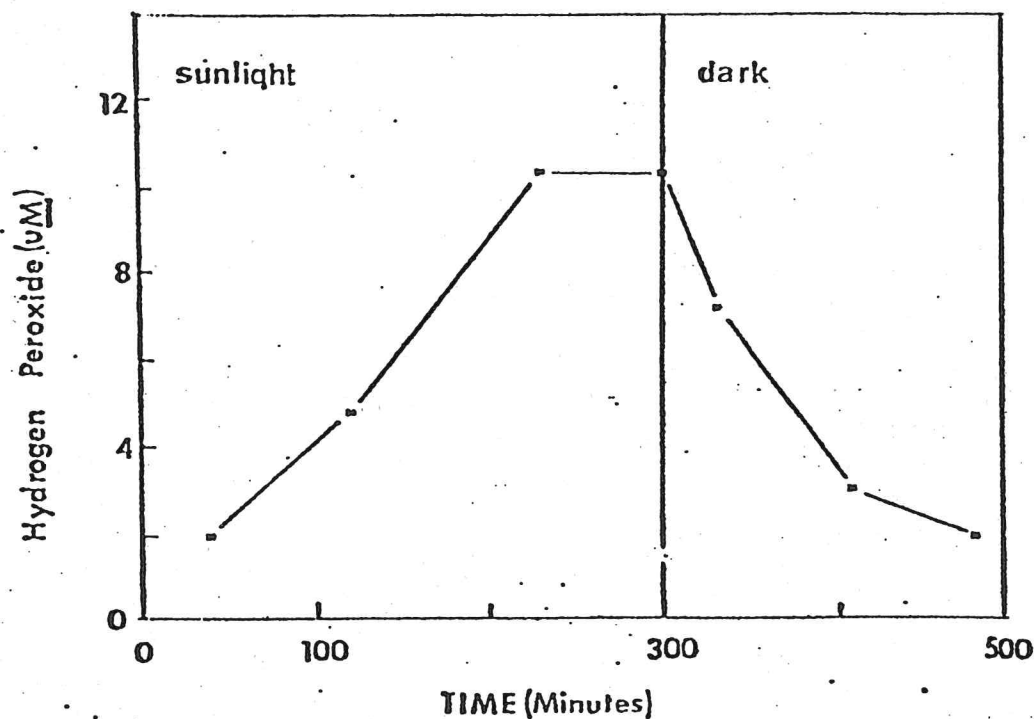


Figure 1. Photooxidant Formation in a Sunlight Irradiated Field Water Sample and Dissipation of the Oxidant in the Dark.

Hydrogen peroxide absorbs sunlight and photodecomposes. The photolysis of hydrogen peroxide apparently results in the formation of hydroxyl radical, an extremely potent oxidizing agent. Unbuffered solutions containing hydrogen peroxide (100 micromolar) and eight pesticides used on rice were exposed to sunlight in sealed flasks. The rate of breakdown of the pesticide was measured and compared with dark control solutions. The following table summarizes results:

Effect of Hydrogen Peroxide on Pesticide Photolysis

| Pesticide | Dark | Half-life (hrs) | Light |
|------------------|---------------|---------------------|------------------|
| | With Peroxide | Light With Peroxide | Without Peroxide |
| Benthiocarb | Stable | 106 | Stable |
| Carbofuran | Stable | 138 | Stable |
| Disulfoton | 350 | 102 | 390 |
| MCPA | Stable | 25 | Stable |
| Methyl Parathion | 600 | 112 | 260 |
| Molinate | Stable | 225 | Stable |
| Parathion | 500 | 122 | 380 |
| Propanil | Stable | 84 | Stable |

The photolysis of each compound examined was clearly accelerated in the presence of hydrogen peroxide. The organophosphates (disulfoton, methyl parathion, and parathion) also showed some breakdown presumably due to hydrolysis. The photolysis rates of MCPA and propanil were remarkably rapid. Photoproducts were not identified except in the case of molinate and benthiocarb where the major products found were those previously identified during photolysis in field water.

B. Objective II. Environmental distribution and dissipation of pesticides in rice fields.

Studies are underway to determine the terminal residues of molinate and benthiocarb in rice field water. The "terminal residues" would be relatively stable chemicals of low toxicity or compounds naturally found in the environment.

A preliminary field test was run with molinate vapor, released at a point, with the air down wind sampled at various distances. This technique has demonstrated photolysis or oxidation of several pesticides, including trifluralin and parathion. While molinate was trapped at downwind sites no definite vapor breakdown products were isolated.

Soil samples from two experimental applications of Bolero 10G have been analyzed for a full year. The dissipation rate in the soil is similar to that obtained with molinate. Initially about 25% of the applied material is found in the top 2" of soil but by harvest time the residue amounts to about 2% of the total applied. One test field was fallow all winter and at flooding time (May) it still contained this small residue of benthiocarb. The other test field was cropped to barley with two flood irrigations due to the dry winter. In early May this field had no detectable residue of benthiocarb. The identify of the soil residues was verified by Gas Chromatography and Mass Specroscopy.

Water from these fields, treated with Bolero 10G, had been collected at intervals after application of the herbicide. This water was analyzed for Benthioncarb, p-chlorobenzaldehyde, p-chlorobenzoic acid and p-chlorobenzyl alcohol. The results are summarized on Figure 2.

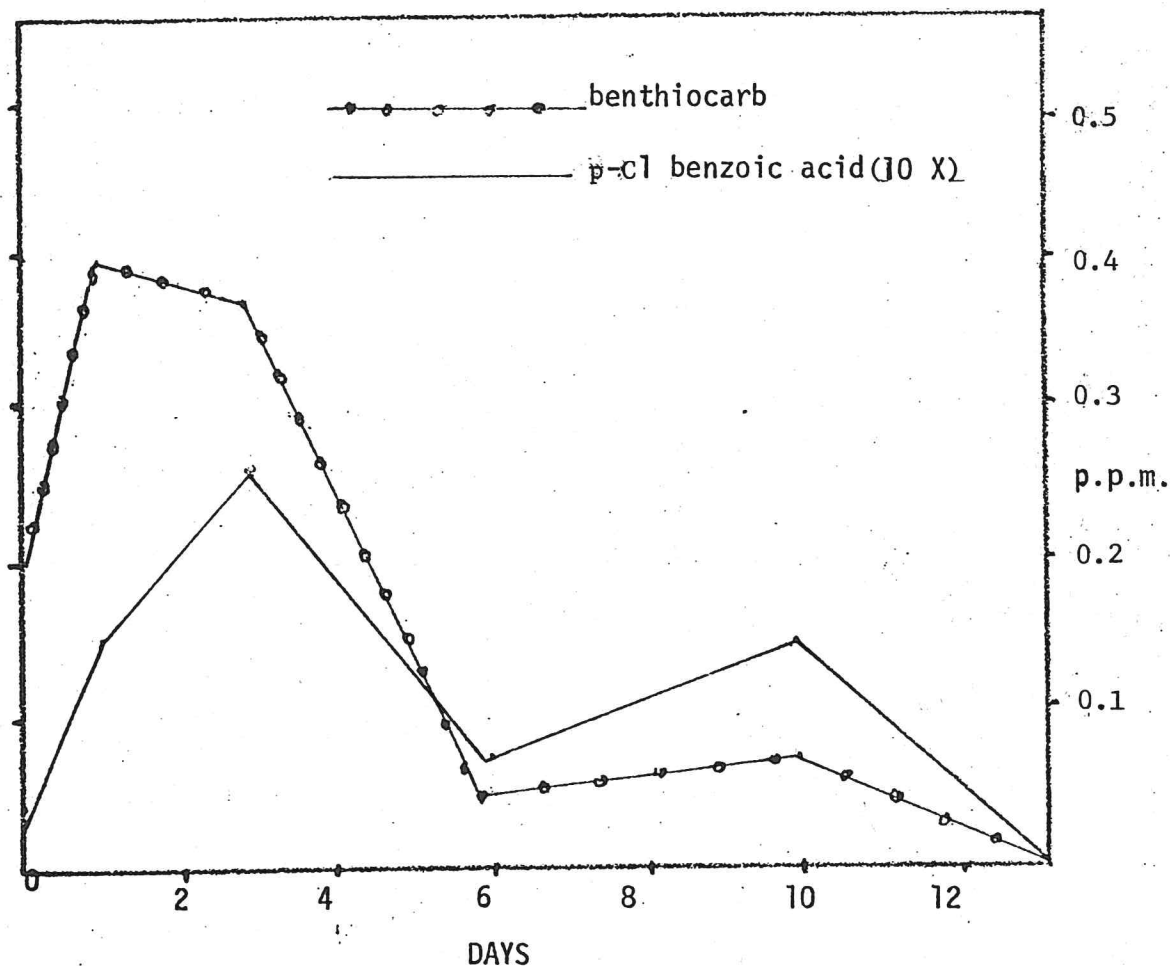


Figure 2. Zall ranch, benthioncarb and p-cl benzoic acid in field water.

Only the water collected immediately after application contained the volatile aldehyde. P-chlorobenzoic acid showed a rise in concentration matching the benthioncarb concentration but lagging a few days behind. No p-chlorobenzoic acid was detected later than 11 days after application.

As of 1976, there was no clear understanding of the environmental fate of TPTH (Triphenyltin hydroxide or Duter). In fact, meetings and correspondence with the Thompson-Hayward Chemical Company indicated that much of the basic physiochemical data was lacking for TPTH and related compounds. Work in our laboratory therefore centered on development of an analytical method capable of measuring TPTH and its suspected degradation products. This method has been successfully used to determine, for example, the solubility and hydrolysis rate of TPTH over a range of temperature and pH--information required for EPA registration. The photodecomposition of TPTH under laboratory and field conditions was examined, again under EPA protocols, with products and disappearance rates ascertained. Initial results of these studies indicate that TPTH is very insoluble in water (0.5 to 6.6 ppm, depending upon water pH); that it is stable to hydrolysis (no loss at pH 4-10 at 22°C); and that it does photodegrade to less persistent organo-tin species. Studies on the volatilization of TPTH have not been completed.

C. Objective III. Relative importance of environmental factors.

The work with triphenyltin hydroxide will supply information of value to the manufacturer in registering this chemical for use on rice, and to the rice grower in timing and using the fungicide for maximum efficiency and effect.

Oxidant studies indicate a general mechanism for the destruction of organic chemicals in fields, waste water, and drains. This is of great importance in estimating the possible effect of rice pesticides as water pollutants. The naturally occurring oxidants also influence the activity of pesticides in controlling pests and the length of time a pesticide remains effective in the field.

Further studies of volatility may help to control or minimize this major dissipation route for some rice pesticides.

VI. PUBLICATIONS AND REPORTS:

- A. C.J. Soderquist, J.B. Bowers, D.G. Crosby, The Dissipation of Molinate in a Rice Field. J. Agr. Food Chem., 25 940 (1977).
- B. W.M. Draper, "Hydrogen Peroxide, A Photooxidant Generated In Environmental Water." Masters thesis submitted March 1977. University of California, Davis, California.

VII. CONCISE GENERAL SUMMARY OF CURRENT YEARS RESULTS:

The natural oxidant continuously produced by the action of sunlight on pond water is hydrogen peroxide. In sunlight, peroxide acts on many pesticides causing breakdown and decomposition. This natural breakdown mechanism is important in eliminating pesticide residues and limiting the period a pesticide is active. An analytical method for Duter and its metabolites was developed and its breakdown and transport in the environment is being studied. Bolero (benthiocarb) herbicide dissipation in

rice fields is due to volatilization, photochemical breakdown and soil adsorption. The residue on the soil gradually breaks down during the growing season, with a very small residue carrying over into the next season. Volatilization rate of Ordram (molinate) from water varies with water temperature but is not effected by wind.