

COMPREHENSIVE RESEARCH ON RICE

ANNUAL REPORT

January 1, 1976 - December 31, 1976

I. PROJECT NUMBER AND TITLE: RP-5, Environmental Fate of Pesticides Important in Rice Culture.

II. PROJECT LEADERS AND PRINCIPAL U.C. INVESTIGATORS:

Project Leader: D.G. Crosby, Professor; J.B. Bowers, Staff Research Associate
IV. Principal U.C. Investigators: C.J. Soderquist, Staff Research Associate
II; William Draper, Research Assistant. Other U.C. Cooperators: A.S. Wong, Research Assistant; R.D. Ross, Predoctoral Trainee.

III. LEVEL OF 1976 FUNDING: \$22,000.

IV. OBJECTIVES ACCORDING TO 1975 PROPOSALS AND EXPERIMENTS BY LOCATION CONDUCTED TO ACCOMPLISH THESE OBJECTIVES:

- A. Objective I. To investigate and identify environmental factors which govern transport and chemical transformations of rice pesticides.
1. Molinate: Identification of, and analytical methods for, environmental breakdown products; volatilization experiments; breakdown of molinate vapor; chemical oxidation experiments; air and soil analysis (UCD).
 2. Benthioncarb: Identification of breakdown products; analytical methods; synthesis and reactions of breakdown intermediates; volatilization rates and breakdown rates (UCD).
 3. Parathion: Breakdown products from vapor (UCD).
 4. Natural oxidants in rice fields: General analytical method development; analysis of natural waters; survey of oxidant chemicals; photooxidation of various rice pesticides; isolation of hydrogen peroxide as oxidant (UCD).
- B. Objective II. To examine the environmental distribution and dissipation of these chemicals in rice fields.
1. Molinate (Ordram): Soil sampling for analysis (Sutter Co.); air sampling (Sutter Co.); sampling of aquatic breakdown products for analysis (Sutter Co.).
 2. Benthioncarb (Bolero): Sampling of air, water, soil for analysis (Sutter and Yuba Co.).
 3. Parathion: Application and air-sampling of parathion (San Joaquin Co.).

C. Objective III. To estimate the relative importance of the factors to field applications.

1. Comparison of dissipation rates, volatilization, and degradation of molinate and benthocarb (UCD).
2. Testing of molinate sulfoxide on rice and rice weeds (UCD test plots).

V. SUMMARY OF CURRENT YEAR'S WORK BY OBJECTIVE:

A. Objective I. Environmental Factors which Govern Transport and of Rice Pesticides.

The remaining photodecomposition products of molinate, formed by laboratory irradiation of aqueous molinate in the presence of tryptophan sensitizer, were identified. By subsequent irradiation of key intermediates, an approximate degradation pathway (Fig. 1) could be proposed, showing molinate breakdown to be primarily (and perhaps exclusively) hydrolytic and oxidative with formation of molinate sulfoxide the key step. Analytical methods for major breakdown products were established and applied to the laboratory photolysis mixtures (Fig. 3); more than 90% of the molinate was accounted for at each sampling time.

Irradiation of molinate vapor without additional oxidants resulted in quantitative recovery of unchanged starting material. However, addition of excess oxidant caused rapid breakdown, and 2-oxomolinate was identified as a major product. Extensive modification of the vapor-phase photochemical equipment and technique is underway to permit oxidation experiments in the presence of more typical environmental concentrations of ozone, nitrogen oxides, and other atmospheric oxidants. Atmospheric breakdown of molinate by light and oxidants appears likely but must be substantiated.

Photolysis of aqueous benthocarb was investigated in the laboratory in the same way as molinate. Again, no significant breakdown occurred in pure water, but photodecomposition was rapid in the presence of tryptophan or heat-sterilized rice-field water. The half-life in the reactor was about 8 hours (compared to molinate's 10 days), but the products were entirely analogous (Fig. 4)--photo-oxidation to form benthocarb sulfoxide was the key step. However, the p-chlorobenzylsulfonic acid (corresponding to molinate's ethane-sulfonic acid) proved to be unstable, and the sulfone decomposed to p-chlorobenzyl alcohol, p-chlorobenzaldehyde, and p-chlorobenzoic acid; considerable difficulty was encountered in the synthesis of the sulfonic acid due to its reactivity. Over the first few days, at least, photodecomposition of benthocarb is far more significant than microbial metabolism.

Volatilization rates of benthocarb were determined at several temperatures; this herbicide is less volatile than molinate (half-life at 25°C, 8.6 days compared to 3.0 days), although its volatilization also increases rapidly with increasing temperature (Fig. 5). The

presence of soil, added to aqueous solutions of molinate, did not alter volatilization rates significantly.

The vapor-phase photodecomposition of parathion was examined with and without added oxidant; the insecticide was readily converted to the very toxic paraoxon and p-nitrophenol in the presence of ozone or surfaces but was stable otherwise. It also was stable to irradiation in rice-field water over the period of the experiment. (The corresponding P-S bond of disyston also was stable to oxidation under these conditions, but the C-S-C group was oxidized to the sulfoxide.)

A sensitive analytical method was developed for oxidants occurring in water. In the presence of hydrogen peroxide or a number of other oxidizing agents, leuco-crystal violet reagent was oxidized quantitatively to a dye which absorbs strongly at 596 nm. The method is sensitive to 10^{-6} M (0.03 ppm) based on H_2O_2 , and response is linear from less than 10 to over 200 μ M. Air does not interfere, but otherwise the response does not differentiate between H_2O_2 , peracids, and probably certain hydroperoxides.

About 50 natural water samples were collected in Northern California, transported and held in the dark at ambient temperature, portions were exposed to summer sunlight for 5-8 hours, and the irradiated and dark samples were analyzed. The summarized results (Table I) show that almost all samples generated significant photooxidant levels, while no oxidant generally was detected in the controls. The half-life of oxidant activity was on the order of one hour, and samples slowly lost oxidizing ability during several days of irradiation. Distilled water solutions of a variety of substances were tested for photooxidant generation by sunlight, a few of which are listed in Table II. As reported previously (1975 Report), tryptophan and tyrosine showed strong activity, as did several other materials. No pattern or relation of structure to activity is apparent yet.

Buffer solutions (pH 7.0) containing 100 mg/l of L-tryptophan and 100 mg/l of each of several common pesticides were irradiated in the closed laboratory photoreactor. Samples were collected at intervals, analyzed by glc according to standard procedures, and the rate of loss compared to that of a dark control (Table III). No obvious photoproducts were observed. PCP and nitrofen photolyzed rapidly, and tryptophan did not seem to affect the rate; this is not surprising, in that the initial photolysis step is a photonucleophilic displacement in both instances. The photolysis rate of 2,4,5-T may have slowed slightly due to competing light absorption by the tryptophan, although no really significant effect was observed. However, propanil photolysis was clearly accelerated by tryptophan, and molinate photolysis was very significant.

B. Objective II. Environmental Distribution and Dissipation of Pesticides in Rice Fields.

The analytical methods for major molinate photoproducts were applied to water samples from a rice field which had received a commercial application of Ordram 10G (granular) formulation (Fig. 3). Whereas

the photoproducts had appeared to be rather stable under laboratory conditions, they did not persist in the field, perhaps due to microbial action and volatilization. Air above the field was sampled before and at several times immediately after application; although low levels of molinate were present in the atmosphere for many hours following treatment, no breakdown products could be detected. A full year's soil samples from the field were collected and analyzed (Fig. 2) and showed dissipation of molinate residues, presumably by volatilization and microbial action. However, a consistent molinate level of 0.1 ppm persisted throughout the year at depths down to 12 inches.

Commercial applications of Bolero (10% granular benthicarb) were monitored at fields near Robbins and Marysville; the benthicarb dissipation (Fig. 6) was similar to that of molinate at the Marysville location but a little slower at Robbins, perhaps due to differences in water temperature. cursory initial examination of water for Bolero breakdown products revealed p-chlorobenzoic acid but soil analysis has not been completed.

In connection with another project, parathion was applied by ground-rig as a standard spray (EC) formulation in the San Joaquin Valley. Air samples taken at distances up to one mile downwind revealed increasing conversion of parathion to paraoxon and p-nitrophenol directly correlated with distance and exposure to sunlight. These results also might be expected to apply to the use of parathion (and probably methyl parathion) on rice but will require further verification.

C. Objective III. Relative Importance of Environmental Factors.

Of the three pounds per acre of molinate applied to a flooded rice-field, over 90% was released to the water during the first 2 days after application, and 8% was taken up by soil. However, the rapid volatilization from water and slower release from soil eventually resulted in losses of up to 80% of the herbicide to the atmosphere. Photooxidation in field water amounted to about 5%, plant uptake to about 5%, and the remainder was found in soil or was unaccounted for.

The

The photochemical decomposition of both molinate and benthicarb in water depended upon the presence of natural oxidants. Benthicarb decomposed much more rapidly than molinate; both appeared to result eventually in products nontoxic to both animals and plants. Decomposition in the atmosphere also may depend upon photooxidation and is under investigation.

Photooxidation of many types of pesticides by stable oxidants generated in rice-fields may be an important general phenomenon; however, there also is evidence of the generation of even more powerful but short-lived oxidants. While some oxidation will result immediately in less-toxic products, the rice-field oxidation of benthicarb and molinate result in sulfoxides which have been suggested to be even more potent herbicides than are the parent compounds [Casida et al., Science 184, 573 (1974)]. Laboratory experiments showed that molinate also could be oxidized to sulfoxide intentionally in the spray-tank

by addition of hypochlorite. In an initial experiment, pure molinate sulfoxide was synthesized and tested, in comparison with molinate, for herbicidal action in a rice-field test plot; both compounds dissipated in a single day to levels below detectability, and weed-control was indeterminate.

VI. PUBLICATIONS OR REPORTS:

- A. W.M. Draper, D.G. Crosby, J.B. Bowers, Measurement of photochemical oxidants in agricultural field water. Paper presented at the 172nd National Meeting, Amer. Chem. Soc., San Francisco, Sept. 1, 1976.
- B. C.J. Soderquist, J.B. Bowers, D.G. Crosby, Photodecomposition of molinate. Paper presented at the 172nd National Meeting, Amer. Chem. Soc., San Francisco, Sept. 1, 1976.
- C. J.B. Bowers, C.J. Soderquist, D.G. Crosby, Distribution and fate of molinate in a rice field. Paper presented at the 172nd National Meeting, Amer. Chem. Soc., San Francisco, Sept. 1, 1976.
- D. C.J. Soderquist, J.B. Bowers, D.G. Crosby, The dissipation of molinate in a rice field. J. Agr. Food Chem., 25, in press (1977).
- E. D.G. Crosby, R.D. Ross, J.B. Bowers, Photodecomposition of benthocarb. J. Agr. Food Chem., submitted for publication.

VII. CONCISE GENERAL SUMMARY OF CURRENT YEAR'S RESULTS:

The rapid dissipation of molinate (Ordram) and benthocarb (Bolero) from flooded rice fields is due primarily to volatilization into the atmosphere and secondarily to light-induced chemical decomposition in the water. Natural oxidants generated in water initiate the breakdown, possibly to useful herbicidal products. Decomposition of benthocarb is much more rapid than that of molinate, but overall dissipation rates for these herbicides appear to be about the same. Parathion is oxidized in the air above treated fields, but no atmospheric breakdown products of molinate could be detected.

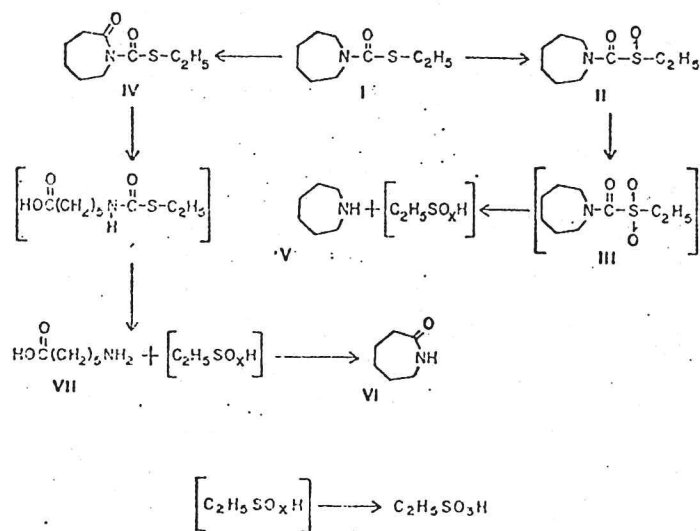


Fig. 1. Molinate breakdown products

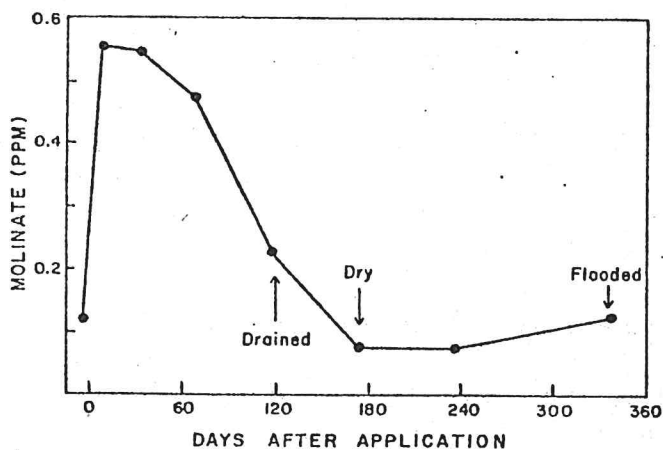


Fig. 2. Molinate soil residues

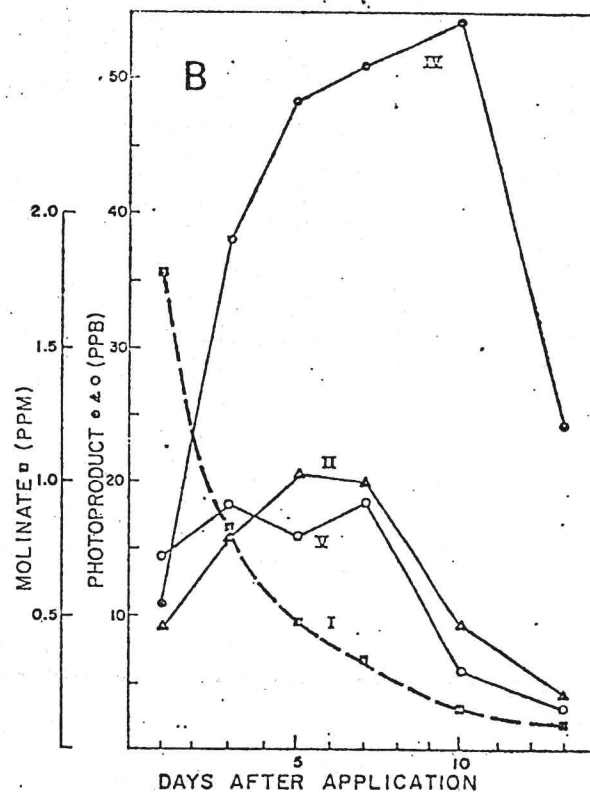
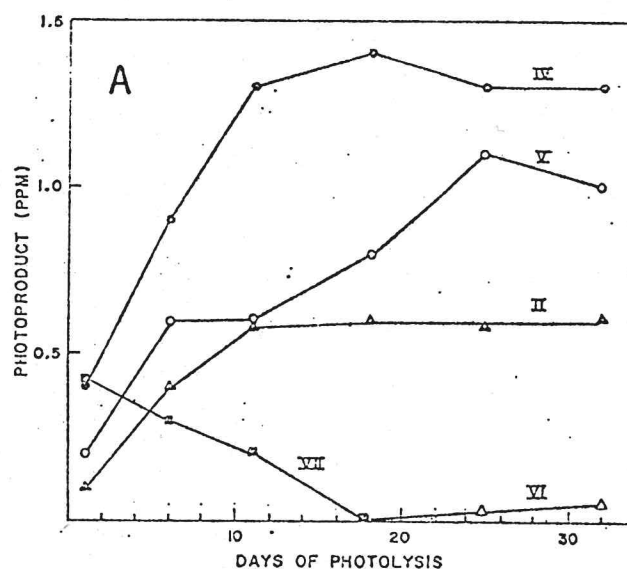


Fig. 3. Analysis of molinate breakdown products in the laboratory (A) and rice field (B)

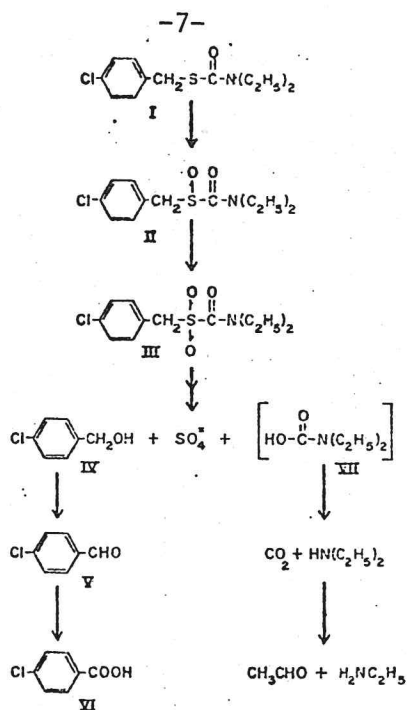


Fig. 4. Benthicarb breakdown products

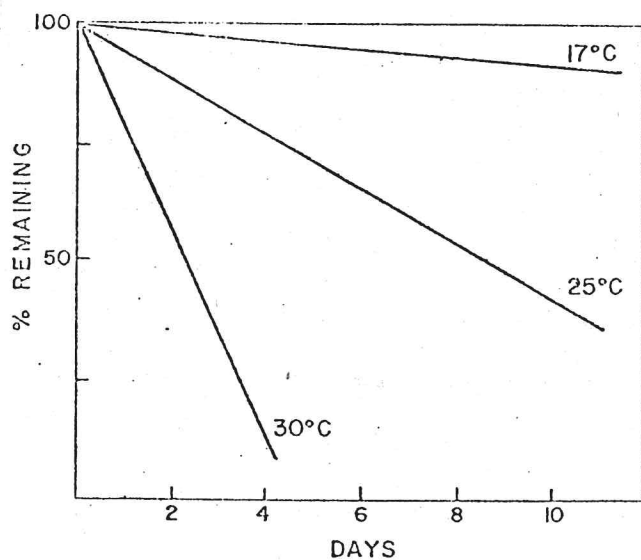


Fig. 5. Benthicarb volatilization

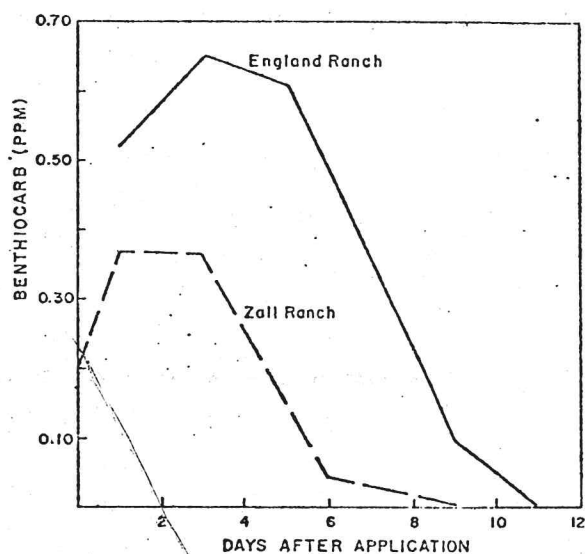


Fig. 6. Benthicarb dissipation in rice fields.

Table I
Photooxidant in Natural Water^a

Source	H ₂ O ₂ Equivalents (μM)
Rice fields	3.8 (<1 - 8.5)
Irrigation ditches	3.8 (<1 - 6.9)
Corn field irrigation	3.4 (2.6 - 5.3)
Streams (Yolo County)	2.5 (2.2 - 3.0)
Sewage ponds (Davis)	24 (11 - 38)
Sewage settling tank (Davis)	<1
Drinking water (Davis)	<1
Sea water (Santa Cruz)	1.0 (<1 - 3.9)
All controls	<1

Table II
Photooxidant Generators

Compound	mM	H ₂ O ₂ Equivalent (μM)
n-Amyl alcohol	1.14	- ^a
Aniline	1.07	7
Benzaldehyde	1.00	-
Benzoic acid	1.00	-
Benzophenone	1.00	19
Chlorophyll	100 ppm	-
p-Cresol	1.00	17
Phenol	1.06	-
Stearic acid	0.33	-
Tryptophan	1.00	>42
Tyrosine	0.55	25

^aNot significantly different from control (<1).

Table III
Effect of Tryptophan (Try) on Herbicide Photolysis^a

Herbicide (10 ppm)	Half-life (hrs)		
	Dark	With Try (100 ppm)	Without Try
PCP	Stable	3.8	3.8
Nitrofen	Stable	4.0	4.0
2,4,5-T	Stable	32	30
Propanil	Stable	50	120
Molinate	>1000	240	Stable