

COMPREHENSIVE RESEARCH ON RICE
ANNUAL REPORT
January 1, 1979 - December 31, 1979

PROJECT TITLE: The Environmental Fate of Pesticides Important to Rice Culture

PROJECT LEADER AND PRINCIPAL UC INVESTIGATORS:

Project Leaders: D.G. Crosby and J.B. Bowers
Principal Investigators: J.B. Bowers, W.M. Draper, and K. Linton
In collaboration with J.N. Seiber and J.E. Woodrow (molinate) and D.E. Bayer (Drepamon).

LEVEL OF 1979 FUNDING: \$22,930 (including \$2000 carryover).

OBJECTIVES AND EXPERIMENTS CONDUCTED BY LOCATION TO ACCOMPLISH OBJECTIVES:

- A. Objective I. To identify and investigate the environmental factors which govern movement and chemical transformations of rice pesticides.
 - 1. Measure laboratory volatilization rates of herbicides (UC Davis).
 - 2. Measure photodegradation of pesticides and identify products (UC Davis).
 - 3. Degradation of molinate vapor (UC Davis; fields in Yolo and Sutter Co.).
 - 4. Measure pesticide hydrolysis and other environmental factors (UC Davis).
 - 5. Determine formulation properties and degradation (UC Davis).
- B. Objective II. To estimate and relative importance of each factor to the practical use of specific rice pesticides.
 - 1. Movement and photolysis of formulated DuTer (UC Davis).
 - 2. Relative volatility of molinate, thiobencarb, and Drepamon (UC Davis).
 - 3. Photolysis of Drepamon and MCPA amine (UC Davis).
- C. Objective III. To apply research results toward registration and improved management of rice pesticides.
 - 1. Collect and transmit environmental registration data for DuTer and Drepamon (UC Davis).
 - 2. Compare volatility of thiolcarbamates (molinate, benthocarb, drepamon) (UC Davis).
 - 3. Degradation rate of MCPA amine formulation (UC Davis).

SUMMARY OF 1979 RESEARCH (MAJOR ACCOMPLISHMENTS) BY OBJECTIVE:

- A. Objective I. To identify and investigate environmental factors which govern the physical and chemical transformations of rice pesticides.

1. Thiolcarbamates. Our previous reports have shown the importance of volatilization in the loss of molinate (Ordram) and Thiobencarb (Bolero) from treated rice fields. According to Drs. Bayer and Seaman, Drepamon--a relatively new thiolcarbamate herbicide--appears very promising, and so its volatility was compared to that of the other two. At a constant temperature typical of field application conditions (24.5°C), pure drepamon proved much the more volatile (Fig. 1), with a relative half-life of about 1 day compared to molinate (3 days) and thiobencarb (6 days).

Although the photodegradation rates of the thiolcarbamates in the presence of oxidant (H_2O_2) were reported to be similar (1978 Report), more detailed examination showed that drepamon (I) actually was also the most rapidly degraded (half-life 20 hours in the indoor photoreactor) compared to molinate (30 hours) and thiobencarb (40 hours) (Fig. 2A). The thiolcarbamates remain relatively stable in the dark and in pure water (Fig. 2B), although some drepamon was lost by volatilization and by slow reaction with the oxidant. Extensive analytical method development, isolation and characterization studies, and synthesis of standards led to identification of a series of photolysis products (Fig. 3) which fit a pattern consistent with those formed from molinate and thiobencarb (1976 and 1977 Reports).

The principal extractable photoproducts were II, III, and IV (Fig. 4), while V quickly formed VI, but at 5 hours they accounted for less than 30% of the decomposed drepamon. Most of the rest eventually may be represented by the identified sulfonate, IX, which remained unextractable even at pH 2. Although no ^{14}C -drepamon was available, and the unextractables could not be analyzed directly, a very similar experiment with ^{14}C -thiobencarb showed the same rapid increase in unextractable photoproducts (Fig. 5) of which the major constituent was the corresponding 4-chlorobenzylsulfonic acid.

Despite its relative stability in the indoor photoreactor, drepamon (in a transparent sealed container) photodecomposed in sunlight even in pure water (about 30% in 7 days), with the sulfoxide (V) and benzaldehyde (VI) as major extractable products. It is expected that unvolatilized drepamon remaining in solution in treated rice fields would decompose eventually to VI, VII, and IX (the "terminal residues"). A limited field test was conducted at UCD (with collaboration of D.E. Bayer), where Drepamon 5G was applied at 3 lbs ai/acre to a 200 ft² enclosed rice plot flooded to 4 inches. Water and soil were sampled at intervals, control samples were fortified with drepamon standard, and drepamon was analyzed by gas chromatography (GLC) with an N-specific detector. Analytical recoveries were poor (50%), but the herbicide was observed to dissipate with an interim half-life of about 2 days (compared to 3 days for molinate and 4 days for thiobencarb under thoroughly similar conditions). Dissipation from the soil gave a half-life of about 8 days (Fig. 6). Remaining samples have not yet been analyzed for degradation products.

2. Molinate (with J.N. Seiber and J.E. Woodrow). For several years (1977, 1978 Reports), attempts to detect atmospheric degradation of molinate (X) have been unsuccessful. Laboratory experiments indicated that breakdown should be expected; while molinate remained unchanged upon ultraviolet irradiation in air, the presence of small amounts of ozone caused degradation to a series of products (Fig. 7). Rather than continue to sample and analyze air from usual field applications, a cloud of pure molinate was generated on a sunny day and high-volume air samples taken at 2 stations downwind. Analysis of the samples by GLC indicated the presence of two new components corresponding to XI and XII as well as an unknown. Apparently, previous lack of detection has been due to the relatively low concentrations of molinate released from a field at any given time, but as formation of the degradation products requires only individual molinate molecules, atmospheric oxidant, and light the similar degradation of any molinate in the atmosphere seems inevitable.

3. DuTer. The 1978 Report indicated that TPTH--the active ingredient of DuTer--photodecomposed in water, but solid DuTer and TPTH remained unchanged. A question remained as to possible degradation of the actual formulation as it sank or was suspended in water. Duter (47.5% TPTH) was applied at about 2 lbs/acre (4.4 gm/L) to the surface of water in a glass container where it quickly became suspended upon even slight agitation. The stirred mixture was irradiated under outdoor sunlight, water was replaced as it evaporated, and samples were analyzed for TPTH and other tin species.

Within 24 days (the first sample), only 22% of the TPTH was detectable; after 55 days, only 6% remained. A similar experiment with pure TPTH gave 42% remaining after 21 days and 29% after 36 days, starting with only 0.91 mg/L. Thus, it appears that the photodegradation of DuTer is equal to, and perhaps even greater than, that of its fungicidal ingredient.

In light of this rapid mixing and reactivity of TPTH and DuTer in water, it is of interest to know what other chemical transformations they could undergo, especially to product nontoxic products. Attempts to react TPTH with dilute ammonia led only to recovery of starting material. However, TPTH reacts very rapidly and quantitatively with H₂S or sulfide ions in water to form bis(triphenyltin) sulfide (TPTS). TPTS is soluble in organic solvents and is readily extracted from water; it can be separated by thin-layer chromatography, but GLC analysis was not successful. At present, high-pressure liquid chromatography (HPLC) appears promising for eventual analysis of TPTS in field water.

4. MCPA. The major part of this year's Rice Research effort in our laboratory has been on the composition and photodegradation of commercial formulations of 4-chloro-2-methylphenoxyacetic acid (MCPA) dimethylamine salt. This work is reported in detail under Project RP-6 and is only summarized here.

Development of HPLC and GLC analytical methods allowed "MCP-amine" formulations and spray to be analyzed; the only major impurity was 2-methylphenoxyacetic acid. The amine salt, prepared in pure form, proved to be a low-melting solid soluble in organic solvents. The formulation was rapidly degraded in sunlight to give 4-chloro-2-methylphenol and 4-chloro-2-methyl-N,N-dimethylphenoxyacetamide by a new photochemical reaction. The volatile phenols evaporated into the atmosphere, accounting for the observed loss of MCPA.

- B. Objective II. To estimate the relative importance of each factor to practical use of specific rice pesticides.

The drepamon volatilization and field studies indicate that despite its very desirable herbicidal properties, the compound dissipates more rapidly from a treated field than would either the molinate in Ordram or thiobencarb in Bolero. That which remains in water should degrade relatively rapidly. However, this year's limited field test did not account for drepamon loss: the application should have provided about 337 mg/m² at the water surface; at the first sampling time (1 hr.), only 17 mg/m² have been accounted for in water and mud (5%), and a 3 days 10 mg/m² (3%) is present. The possibility that the analytical method is at fault cannot be excluded, but even assuming a 50% error, the largest part of the application was lost rapidly. Quite obviously, an accounting must be made if efficient dremamon use is to be considered.

Although problems in the development of analytical methods precluded the desired field test with DuTer this year, the apparent dissolution and photolysis of its TPTH active ingredient suggests that the fungicide may behave quite differently chemically in the field compared to the laboratory. Both photolysis and the action of dissolved natural sulfur compounds will tend to degrade DuTer. The sinking of the formulation also offers opportunity for microbial degradation which also should limit DuTer's persistence.

Initially, MCPA Amine formulation was expected to be relatively stable. However, based on experiments under artificial conditions, it can be expected to degrade rapidly in sunlight. Also, its presumed non-volatility now must be reassessed in view of its relatively neutral (rather than salt-like) character.

- C. Objective III. To apply research results toward registration and improved management of rice pesticides.

As the environmental-fate data relevant to registration of DuTer has accumulated, it has been provided to the Thompson-Hayward Chemical Company. Similar data for drepamon will be provided to Montedison Company when sufficiently complete. As in the case of molinate, where recognition of the significance of volatility led to development of slow-release Ordram formulations by the manufacturer, it will be important for the producers of both thiobarcarb and drepamon to be persuaded to limit the volatility of their products if consideration for use by rice growers is to continue. Work still is too incomplete

to suggest how the physical and chemical properties of MCPA formulations can be used to provide better herbicide management, but the susceptibility to photolysis provides hope for limited persistence.

PUBLICATIONS OR REPORTS:

D.G. Crosby, J.N. Seiber, J.E. Woodrow, and K.W. Moilanen. Atmospheric degradation of pesticides. Fourth International Congress of Pesticide Chemistry, Zurich, Switzerland, 1978.

C.J. Soderquist and D.G. Crosby. The degradation of triphenyltin hydroxide in water. J. Agr. Food Chem., 27, in press (1979).

W.M. Draper. Pesticide photooxidation in water. Ph.D. Thesis, Univ. of California, Davis, 1979.

CONCISE GENERAL SUMMARY OF CURRENT YEAR'S RESULTS:

As demonstrated by drepamon, molinate, and thiobencarb, laboratory measurement of volatilization rates allow at least a rough estimate of the relative field dissipation rates for the series; drepamon was found to be the least persistent (most volatile) of the three. Drepamon which remains in water or mud is also rapidly degraded and remains as a highly water-soluble, non-extractable product; as indicated by its close relative, molinate, these herbicides can be expected to break down photochemically in the atmosphere following volatilization.

For nonvolatile pesticides such as DuTer and MCPA Amine, the action of sunlight assumes more direct importance in limiting their persistence. In addition to its photochemical degradation, DuTer is seen to react with other natural constituents of water; the rapid degradation of MCPA formulations (in laboratory experiments) is due to both light-catalyzed oxidation and a new chemical condensation reaction, but the effects remain to be verified in the field.

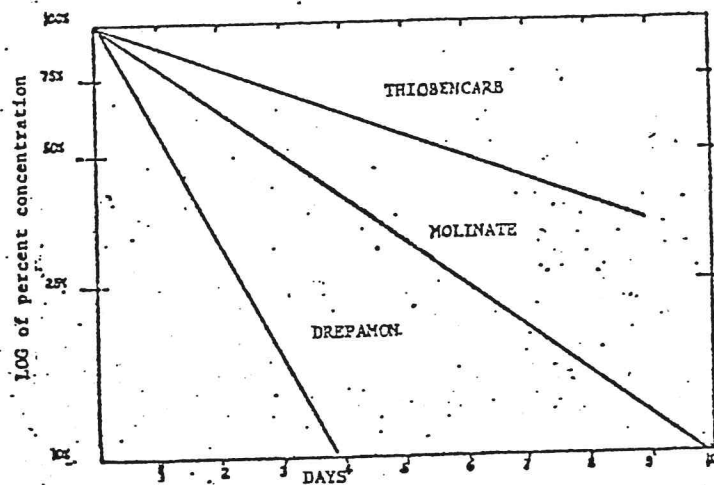


Fig. 1. Volatility loss rates of thiolcarbamate herbicides from water at 24.4°C.

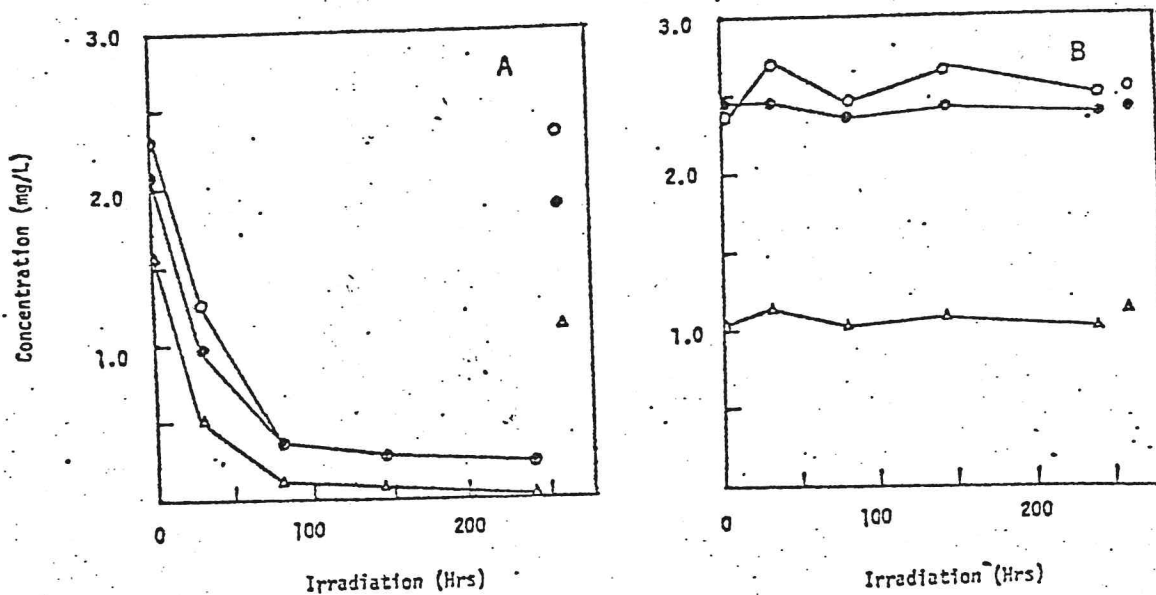


Fig. 2. Thiolcarbamate photolysis in (A) aqueous H₂O₂ and (B) demineralized water. (o) benthioncarb, (●) molinate, (Δ) drepamon. Points on right represent dark controls.

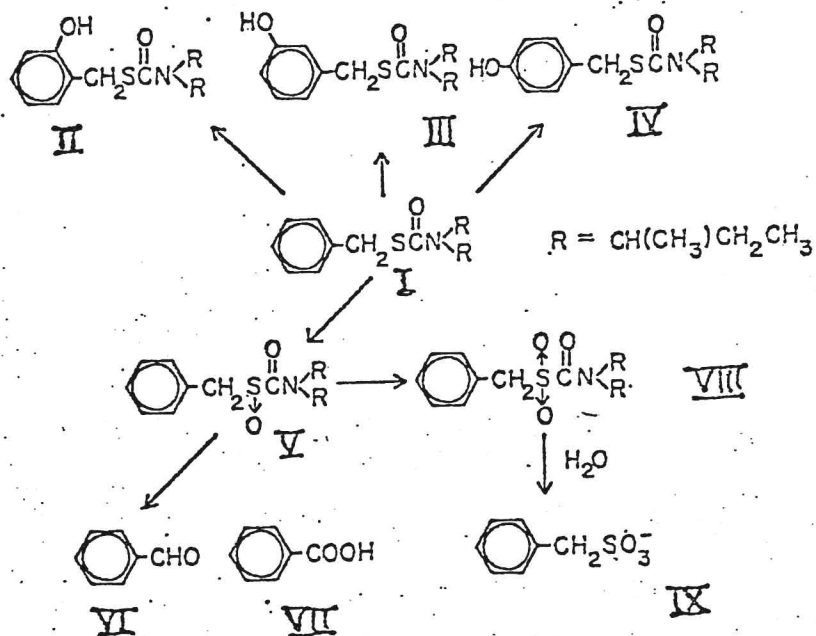


Fig. 3. Proposed photodegradation pathway for drepamon in aqueous hydrogen peroxide.

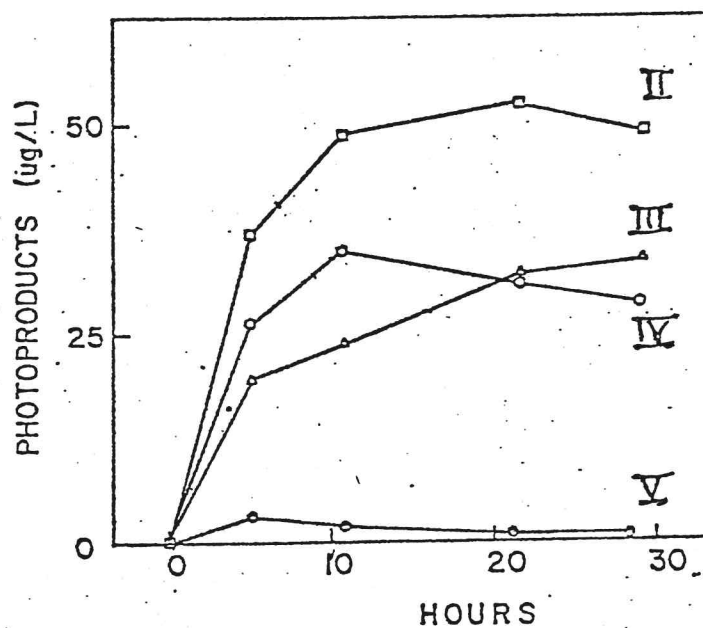


Fig. 4. Drepamon photodegradation (o) and formation of X (o), XX (□), XXI (Δ), and XXII (o) in 30 μM aqueous hydrogen peroxide. (Laboratory photoreactor.)

