

ANNUAL REPORT
COMPREHENSIVE RESEARCH ON RICE
January 1, 1999 - December 31, 1999

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

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OBJECTIVES AND EXPERIMENTS CONDUCTED BY LOCATION TO ACCOMPLISH OBJECTIVES:

Objective I. Identify, investigate, and model environmental factors governing the movement and fate of rice pesticides.

1. Effects of anaerobic conditions on residues of rice pesticides (UCD)
2. Scope and mechanism of anaerobic degradation of carfentrazone-ethyl (UCD)

Objective II. Estimate the relative importance of these factors to practical use of specific rice pesticides.

1. Fate of carfentrazone breakdown products (UCD)
2. Movement of carfentrazone-ethyl and acid in field water (Rice Research Station)
3. Routes of fipronil photodegradation (UCD)
4. Fate of fipronil degradation products (UCD)

Objective III. Apply research results toward meeting regulatory requirements and improved management of rice pesticides.

1. Overall fate of carfentrazone-ethyl in rice fields (UCD, Rice Research Station)
2. Overall fate of fipronil in rice fields (UCD)
3. Replacement for copper as a rice field algicide (UCD).

SUMMARY OF 1999 RESEARCH (MAJOR ACCOMPLISHMENTS) BY OBJECTIVE:

Objective I. Rice field sediments and their interstitial water generally contain relatively little oxygen -- they are anaerobic. Instead of oxidizing pesticides, they may reduce (hydrogenate) them, usually via microbial action. We observed that the acid corresponding to carfentrazone-ethyl was reductively dechlorinated in water -- the sidechain chlorine replaced by a hydrogen atom -- by sunlight and certain reducing agents even in the absence of microorganisms. In view of the the present tendency toward longer flooding of rice fields, our purpose was (1) to model the conditions required for anaerobic reactions of typical rice pesticides, (2) clarify how this photoreduction occurs, and (3) ascertain if the process actually takes place in the flooded fields.

Standard laboratory reduction conditions were established to mimic those which might exist in rice field water, including weakly alkaline or weakly acidic conditions, the presence of hydrogen

sulfide as the principal natural reducing agent, natural quinones that might be expected to occur in field water, and ultraviolet radiation similar to that of sunlight. Most experiments were conducted with carfentrazone acid (Fig. 1A). Under these conditions, very little reduction was observed in the dark, and none in the absence of sulfide.

Under UV irradiation, field water with added sulfide formed 20% of the expected amount of reduction product (the propionic acid); the time required for 50% loss would have required 23 days (that is, a "half-life" of 23 days). With rice straw extract present as well as sulfide, this half-life dropped to about 4 days, while in the presence of the natural quinones juglone and lawsone, it was only a few hours (Fig. 2). Although the reduced forms of the quinones (called hydroquinones) also are powerful reducing agents, they were only marginally effective when tested on carfentrazone acid and could not be recovered from the reaction mixture. The pH of the water was not a major factor.

We propose that the function of the sulfide is to reduce the quinone *in situ* so the resulting hydroquinone can perform the dechlorination before it itself is converted to other products. Quinones and their relatives occur in almost all natural waters, as demonstrated with rice straw extract, and the 2,4-D analog, 4-CPA, also was dechlorinated in this system. While no survey was made of the relative ability of various field waters to carry out the reduction, detection of the propionic acid at several field locations and in successive years suggests that photoreduction may indeed occur.

Objective II. Our 1998 Report indicated that the principal degradation route of carfentrazone-ethyl was its reaction with water to form the corresponding carfentrazone acid (Fig. 1A). Contrary to manufacturer's data, a careful search under both laboratory and field conditions revealed only this and some minor related acids; FMC investigators may have used UV radiation more energetic than that available in sunlight. The 1998 field mobility experiment with Shark® 40D formulation was repeated twice this year, with the same results as before: (1) the herbicidal carfentrazone acid formed rapidly in field water (half-life 11 hours), (2) it then migrated laterally through the soil into adjacent plots, and (3) other than the related propionic, cinnamic, and benzoic acids, no new degradation products were detected, although recoveries were not as good as last year's. A substantial proportion of the propionic acid always was detected in both water and soil, arising perhaps from microbial action as well as by photoreduction.

Fipronil can be accounted for by three major degradation products and at least three minor ones, formed by two separate routes (Fig. 1B). The desthio and sulfonate photoproducts represented by far the major intermediates in the insecticide's breakdown. The former is generated by a concerted free-radical loss of sulfur and the latter by air oxidation, via two different but simultaneous pathways. Both initial products must be considered persistent, although we eventually were able to detect further photodegradation of desthio into the three compounds indicated in Fig. 1B. The sulfonate, which has only low toxicity according to the manufacturer's data, is more prominent than was originally believed, as its detection and measurement previously were difficult.

Objective III. From this year's results, and those of the previous years, the dissipation routes of carfentrazone-ethyl from flooded California rice fields seem clear. The herbicide does not volatilize appreciably from field water but reacts with it rapidly and completely to form carfentrazone acid and its minor dechlorination products. Dissipation from a treated field occurs by lateral migration of the weakly soil-adsorbed acids in the subsurface water, where dilution eventually makes them undetectable. It seems unlikely that they would cross major barriers, but an untreated buffer zone at the field edge probably would be in order.

By contrast, fipronil insecticide is transformed rapidly by sunlight and air into two major and persistent products, desthiofipronil and the sulfonate. The toxic desthio compound is itself slowly degraded, while the water-soluble sulfonate so far appears stable but probably nontoxic.

A literature survey and attempts to design a screening test to find algicides suitable to replace copper sulfate showed the need for a concerted testing program operated primarily by plant

biologists. However, such a program seems feasible and could perhaps involve the USDA Aquatic Weed Research Program at UCD. For example, the nonpersistent, commercially-available quaternary ammonium polyoxyethylene surfactants might be typical candidates for testing.

PUBLICATIONS AND REPORTS

- Crosby, D.G. 1999. Fate of copper sulfate applied to California rice fields. 217th National Meeting, American Chemical Society, New Orleans, LA.
- Ngim, K. K., and D. G. Crosby. 1999. Chloropropionic acid photoreduction. 217th National Meeting, American Chemical Society, New Orleans, LA.
- Ngim, K. K., and D. G. Crosby. 2000a. Chloropropionic acid photoreduction in solutions of Na_2S and Quinones. Submitted to *ACS Symposium Series*.
- Ngim, K. K., S. A. Mabury, and D. G. Crosby. 2000b. The elucidation of fipronil photodegradation pathways. Submitted to *Journal of Agricultural and Food Chemistry*.
- Ross, L., D. G. Crosby, and J. M. Lee. 1998. Use of laboratory, field, and watershed data to regulate rice herbicide discharges, 215th National meeting, American Chemical Society, Dallas, TX.
- Ross, L., D. G. Crosby, and J. M. Lee. 1999. Use of laboratory, field, and watershed data. In *Agrochemical Fate and Transport: Perspectives and Scale of Study*, ACS Symposium Series 751, American Chemical Society, Washington, DC. Chapter 4.

CONCISE GENERAL SUMMARY OF CURRENT YEAR'S RESULTS

1. A 3-year investigation of the fate of carfentrazone-ethyl (Shark®) in California rice fields has been concluded. Negligible amounts of the herbicide dissipated from treated fields via volatilization, soil adsorption, or degradation by sunlight. Instead, it reacts rapidly with field water to produce an acid that is stable, water-soluble, and herbicidal.

2. The carfentrazone acid breaks down to some extent, but most of it moves laterally off-field in the subsurface water flow. Dilution eventually makes it undetectable, suggesting the need for untreated buffer strips between fields. Off-field movement is undesirable.

3. The 4-year investigation of the fate of fipronil (Icon®) in California rice fields also has been concluded. This insecticide is undergoing the registration process, but the principal concern of the California Department of Fish and Game is a toxic and persistent breakdown product formed by sunlight. We have found that this photoproduct itself undergoes breakdown in sunlight to provide low levels of several less persistent compounds. Another major breakdown product, a sulfonate, also has been detected but is considered harmless. We conclude that while more persistent than fipronil, the primary photodegradation products are not permanent and may be tolerated at the low concentrations that exist in the field.

4. Flooded rice soils quickly become anaerobic, and the present tendency toward longer flooding could promote a type of pesticide breakdown quite different from those in the previous, more oxidizing aquatic environment. The anaerobic soils and soil water utilize natural sulfides and quinones to dechlorinate chlorine-containing pesticides, such as carfentrazone acid and 4-CPA, to nontoxic products. However, at environmental concentrations, the reaction may be slow compared to other pesticide dissipation routes.

5. At least one type of nonpersistent algicide, the quaternary ammonium surfactants, might satisfactorily replacement the copper sulfate presently used to treat rice fields. However, a more concerted effort, primarily by plant biologists, will be required in order to establish an adequate algicide screening system.

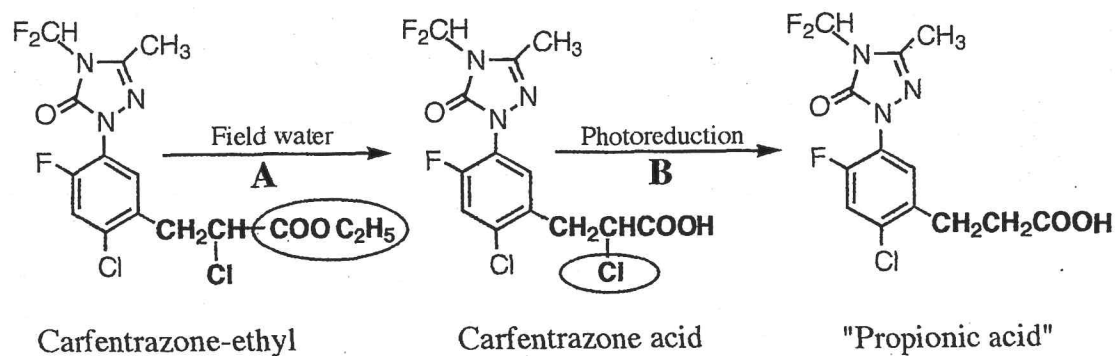


Figure 1A. Hydrolysis (A) and dechlorination (B) of carfentrazone-ethyl (Shark[®]). Structural changes are circled. Reaction B could also be microbial.

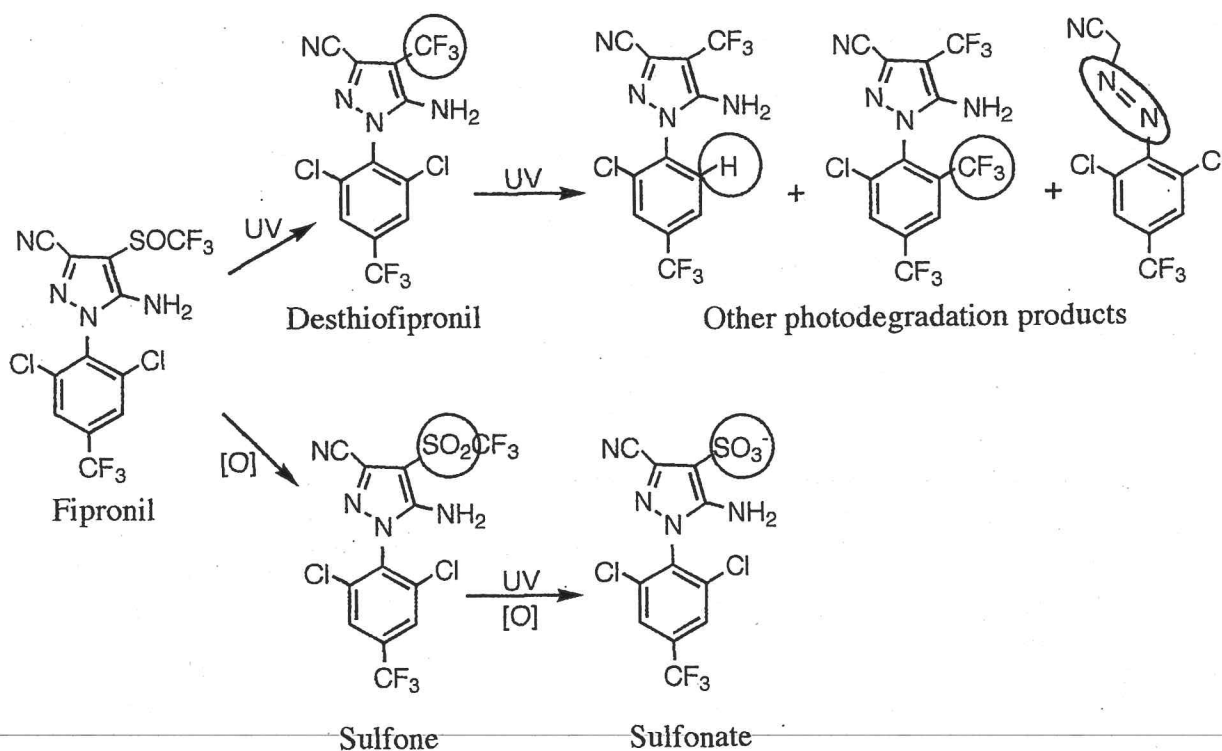


Figure 1B. Routes of fipronil (Icon[®]) degradation in rice field water. Structural changes are circled.

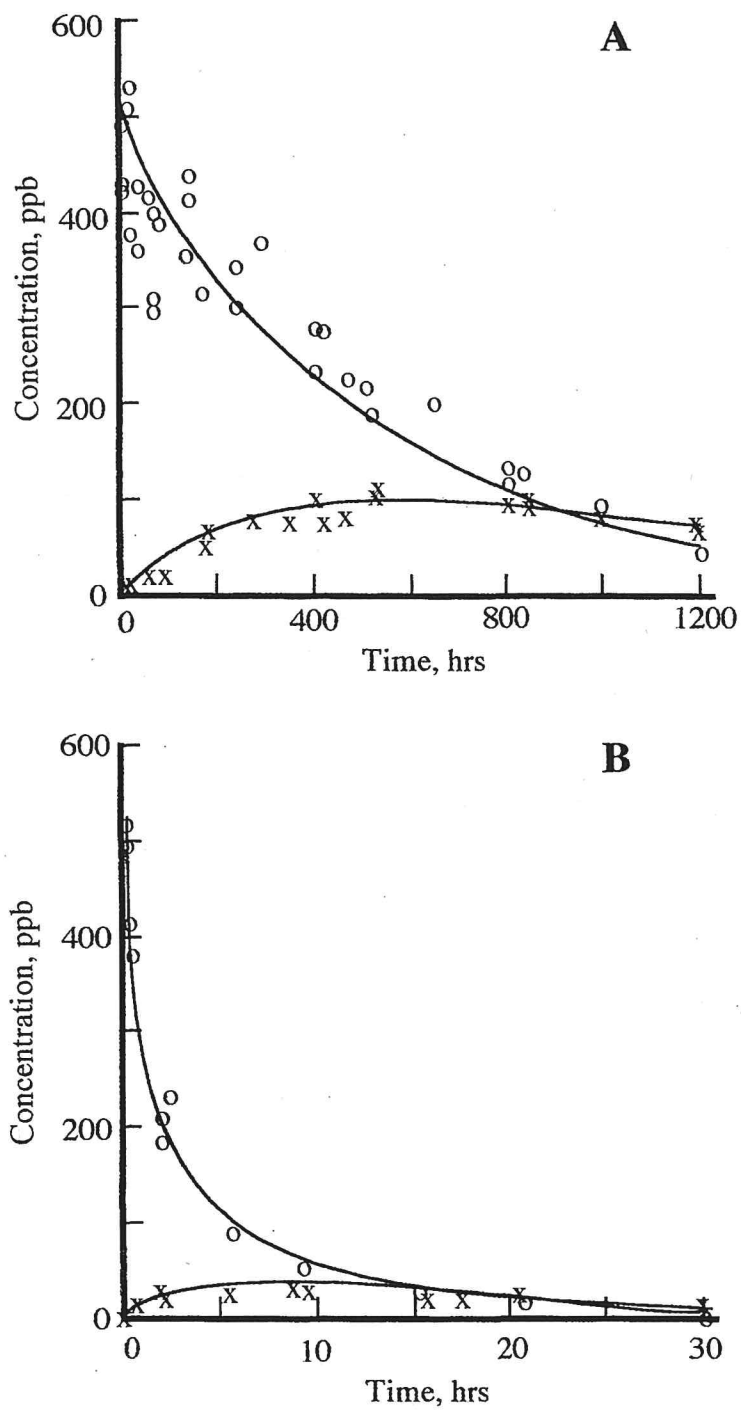


Figure 2. Dechlorination rate of carfentrazone acid (o) and formation of its propionic acid (x) using sulfide only (A) and sulfide plus juglone (B). Note difference in scale.