

ANNUAL REPORT

COMPREHENSIVE RESEARCH ON RICE

January 1, 1997 - December 31 1997

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

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LEVEL OF 1997 FUNDING: \$18,980

OBJECTIVES AND EXPERIMENTS CONDUCTED BY LOCATION TO ACCOMPLISH OBJECTIVES:

Objective I. To identify, investigate, and model environmental factors which govern the movement and fate of rice pesticides.

1. Develop analytical procedures for carfentrazone-ethyl and breakdown products (UCD)
2. Measure carfentrazone-ethyl dissipation rates and products in the field (UCD; Rice Research Station, Biggs; Butte Co. Rice Growers Assn., Richvale)
3. Determine fipronil mass balance: Sulfonate (UCD)
4. Determine the influence of anaerobic conditions on residues of rice pesticides (UCD)

Objective II. To estimate the relative importance of such factors to the practical use of specific rice pesticides.

1. Estimate the volatility of fipronil and its photoproduct from water (UCD)
2. Determine the influence of aquatic oxidants on fipronil persistence (UCD)
3. Measure carfentrazone-ethyl photodegradation under controlled conditions (UCD)

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

1. Compare the persistence of fipronil and its photoproduct between field and lab (UCD; Art Moore Ranch, Butte Co.; Jack Scheidel Ranch, Sutter Co.)
2. Search for a replacement for copper as an algicide (UCD).

SUMMARY OF 1997 RESEARCH (MAJOR ACCOMPLISHMENTS) BY OBJECTIVE:

Objective I.

1. Analysis of Carfentrazone-ethyl. Carfentrazone-ethyl (Shark[®]) is a new experimental herbicide which appears very promising against a broad range of weeds in flooded rice. To evaluate its environmental persistence and fate under California conditions, trace-analysis methods were developed for it and its principal breakdown products in field water and soil that are much

simpler than those provided by the manufacturer (FMC Corporation). Each acidified water sample was passed through a C18 solid-phase extraction column, analytes removed with acetonitrile, and quantitative analysis performed by gas chromatography with a mass spectrometer detector. Soil samples were extracted with acetonitrile, extracts diluted with distilled water, and isolation and analysis conducted as with the field water. Analytical recoveries of carfentrazone-ethyl and major breakdown products were 80-100%, while those of benzoic and cinnamic acids were as low as 40%. The low field-application rates of the herbicide required that the method be accurate down to one part per billion (ppb). For photodegradation experiments, gas chromatography also was used, this time with a nitrogen-specific detector.

2. Field Persistence of Carfentrazone-ethyl. Carfentrazone-ethyl was applied as a flowable formulation at 48 g (1.7 oz, AI) per acre pre-flood in 60 sq. ft. rings set in a larger field at the Rice Research Station at Biggs, CA, and as the same formulation post-flood at 90.7 g (3.2 oz, AI) per acre to 50'x100' fields at the Butte Co. Rice Grower's Association facility at Richvale. Samples of water and soil were collected at intervals and returned to UCD for analysis.

Typical results from the Biggs trials are shown in Fig. 1A. At the low pre-flood application rate, residues of parent herbicide already were below 12 ppb in the first water sample; chemical hydrolysis had rapidly converted it to the corresponding chloropropionic acid, which approached 5 ppb within 8 days. Concentrations of other breakdown products -- the propionic, cinnamic, and benzoic acids -- never reached 5 ppb. In order to avoid continued breakdown in water samples awaiting analysis, a duplicate set of samples was acidified immediately; values are quantitatively slightly higher than those from the untreated samples, but the results are qualitatively the same. They both show that while carfentrazone ethyl is degraded rapidly (half-life 7-23 hours), the much more persistent breakdown products are still at about 2 ppb even after 600 hours (25 days).

Field water residues of carfentrazone-ethyl from the higher post-flood applications at Richvale briefly reached over 100 ppb and again rapidly declined in both types of samples (Fig. 1B). The chloropropionic acid briefly reached 125 ppb, but no breakdown products were detectable at 600 hours. Soil analyses will be completed in early December.

3. Fipronil Mass Balance. Repeated detailed analysis for fipronil and its relatives in field water or water from laboratory experiments failed to show appreciable concentrations of anything other than parent insecticide and its principal photodegradation product. However, as their amounts do not balance that of the fipronil applied, a search for the remainder has been undertaken. One likely breakdown product is the corresponding sulfonic acid, not detected by our gas chromatographic analysis. An alternate analytical method employing high pressure liquid chromatography (HPLC) was devised by which ppb levels of sulfonate could be measured, and analysis of a limited number of samples indicated that it was present but at low levels only.

4. Influence of Anaerobic Field Conditions on Pesticide Residues. Most pesticide residues in field samples have been thought to be formed by oxidation or hydrolysis, but reductive chemical transformations due to anaerobic field conditions have received little attention. As more California rice fields undergo prolonged flooding, the anaerobic reductions of chloro-, nitro-, and sulfoxide-containing pesticides become more likely. The necessary instruments and techniques to investigate environmental factors that govern anaerobic degradations have been assembled and will be used during the coming year to estimate how extended flooding affects pesticide persistence.

Objective II.

1. Volatility of Fipronil and its Photoproduct. Volatilization of rice pesticides from field water often has been the main route for their dissipation, and this has become an important consideration for the registration of new pesticides. However, both the vapor pressure and aqueous solubility of fipronil and its photodegradation product are so low that their volatilization has been

calculated to be negligible. Direct volatility measurements have always been difficult with these types of chemicals, but we have now developed and tested a 10-liter chamber and technique that appears applicable to low-volatility compounds. In this system, the photoproduct indeed appears nonvolatile, but repeated experiments indicate that fipronil actually does volatilize, although slowly. The reason for the discrepancy between calculated and measured values remains unclear but seems to be of considerable concern to fipronil's manufacturer, Rhône-Poulenc Ag Company.

2. Influence of Oxidants on Fipronil Persistence. In previous Reports, we have shown that sunlight-generated oxidants in field water, especially hydrogen peroxide, are important in pesticide degradation. In the sunlight UV reactor, irradiation of a solution containing 460 ppb of fipronil and 7 ppm of hydrogen peroxide reduced the insecticide's half-life from >24 hours to less than 1 hour, while that of the persistent fipronil photodegradation product also dropped from >50 hours to less than 1 hour. While photooxidants do not reach ppm levels in field water, they may still be important for fipronil breakdown and offer a way to destroy the residues if need be.

3. Photodegradation of Carfentrazone-ethyl. To determine the factors responsible for the field dissipation of carfentrazone-ethyl, solutions containing 220 ppb of the herbicide (corresponding to an application of 90 grams/acre) in pH 7 phosphate buffer or 263 ppb in pH 7 rice field water were irradiated with UV light in a sunlight simulator and samples analyzed periodically. In the buffer, carfentrazone-ethyl dissipated with a half-life of 40 hours (1.7 days, Fig.2A) with the proportionate formation of the chloropropionic acid and only very low levels of other degradation products; at 82 hours, about 25% of the initial herbicide still remained. Dissipation of the herbicide and generation of acids also occurred in dark controls (Fig. 2B), although at a much lower rate (half-life 123 hours), indicating that hydrolysis -- reaction with water -- indeed was a key factor.

Repetition of the experiment using freshly-collected pH 7 field water reduced the carfentrazone-ethyl half-life to 31 hours, closer to that observed in the field (Fig. 3A). However, even in the dark, field water caused loss of carfentrazone-ethyl with about the same half-life (27 hours, Fig.3B), simultaneous formation of the chloropropionic acid, and negligible amounts of the expected cinnamic acid, just as in light. As these experiments were conducted in sealed containers, volatilization was not a factor, and the results suggest that hydrolysis is the most important factor in the herbicide's field dissipation -- a reaction with the water that proceeds regardless of sunlight.

Objective III.

1. Fipronil Persistence. Fipronil insecticide still appears very promising for control of rice water weevils, although its rapid breakdown in UV to a highly persistent and toxic product raised concern over the insecticide's proposed use on paddy rice. To reexamine this persistence, Fipronil 80WDG was applied at 15.9 grams/acre AI, pre-flood-incorporated, to 2.65 acres of an 8 acre field (Scheidel Ranch, Sutter Co.). The entire field was flooded about 30 hours later, with slow release to adjacent areas -- a situation similar to those of previous experiments. Soil analysis showed a maximum fipronil level of 10 ppb which declined to 6 ppb over the course of 17 days, but no residues of either fipronil or its photoproduct were detectable in the water down to 1 ppb. To account for this dilution and movement of residues, the same fipronil application was made within 30'x30' metal rings (Art Moore Ranch, Butte Co.). Dissipation curves were similar to those from previous years, with a fipronil half-life of 22 hours in water (Fig. 4A) and 460 hours in soil (Fig.4B), and rapid formation of photoproduct and its subsequent dissipation (half-life 60 hours). It appears that in commercial practice, a combination of environmental and physical factors may interact to lower fipronil residues in water to below detectability. The photoproduct dissipates.

To examine the formation and persistence of the fipronil photoproduct under more controlled conditions, a relatively high fipronil concentration in water (800 ppb) was irradiated in the UV photoreactor. The insecticide level declined with a half-life of about 8 hours, and photoproduct reached a maximum of 400 ppb within about 25 hours. However, irradiation of photoproduct by itself resulted in steady loss and a half-life of about 180 hours (7.5 days) under

these conditions; surprisingly, no degradation products could be detected. However, sunlight obviously is an important factor in the persistence of fipronil's photoproduct.

2. Alternatives to Copper as an Algicide. The continuing annual addition of copper to California rice fields, primarily in the form of bluestone, inevitably will raise soil copper levels to a point where the crop is damaged. Through a literature search and local discussions, several potential candidate replacements have been identified, including carfentrazone, sodium endothall, polyoxyethylene (di-methylimino)ethylene dichloride, and sodium hypochlorite. While all except of the first are toxic to fish at elevated concentrations, a safe algicidal concentration might be found which also would be safe for the rice. The important finding is that there indeed may be feasible low-toxicity alternatives that would control algae without damage to the rice field environment.

PUBLICATIONS AND REPORTS

Ngim, K. K., D. G. Crosby, and S. A. Mabury. 1997. The photodegradation of fipronil in water. Abstr. 18th Annual Meeting, SETAC, San Francisco, CA, 18 November 1997, p. 23.

CONCISE GENERAL SUMMARY OF CURRENT YEAR'S RESULTS

1. The experimental herbicide, carfentrazone-ethyl (Shark[®]), dissipates from treated rice fields within about 2 days, but its more persistent chloropropionic acid and other acidic breakdown products still are detectable at substantial levels in water as much as a month after herbicide application. Reaction with the is the main carfentrazone-ethyl breakdown route, and sunlight is a relatively unimportant factor. While the breakdown products are not presently considered particularly toxic to animals, the chloropropionic acid is somewhat phytotoxic; its movement and fate may warrant further investigation. All together, carfentrazone-ethyl so far appears environmentally suitable for rice field use.

2. Sunlight-energized breakdown has been confirmed as the principal dissipation route for the experimental insecticide fipronil (Icon[®]) in water. This year's work confirmed that a single photolysis product was the only significant breakdown product detectable in field or laboratory experiments, although low levels of a corresponding sulfonate and possibly the amide also are present.

3. Although fipronil's toxic photoproduct was shown to dissipate more slowly in water than does the parent insecticide (half-lives of about 2 days and 1 day, respectively), none of its breakdown products were detected under either field or lab conditions. Breakdown of both it and fipronil was greatly accelerated in the presence of the common rice field oxidant, hydrogen peroxide, providing a possible key to controlling residues. A method devised to estimate the evaporation of low-volatility chemicals from field water indicated that fipronil volatilizes slowly, while the photoproduct appears to be nonvolatile. Fipronil dissipated by half within about 20 days in flooded soil, and the insecticide's environmental properties are deemed acceptable so far.

4. The emergence of several candidate algicides indicates that control of rice field algae might be possible without the use of toxic and persistent copper compounds.

Donald G. Crosby
Project Leader

12/5/97
Date

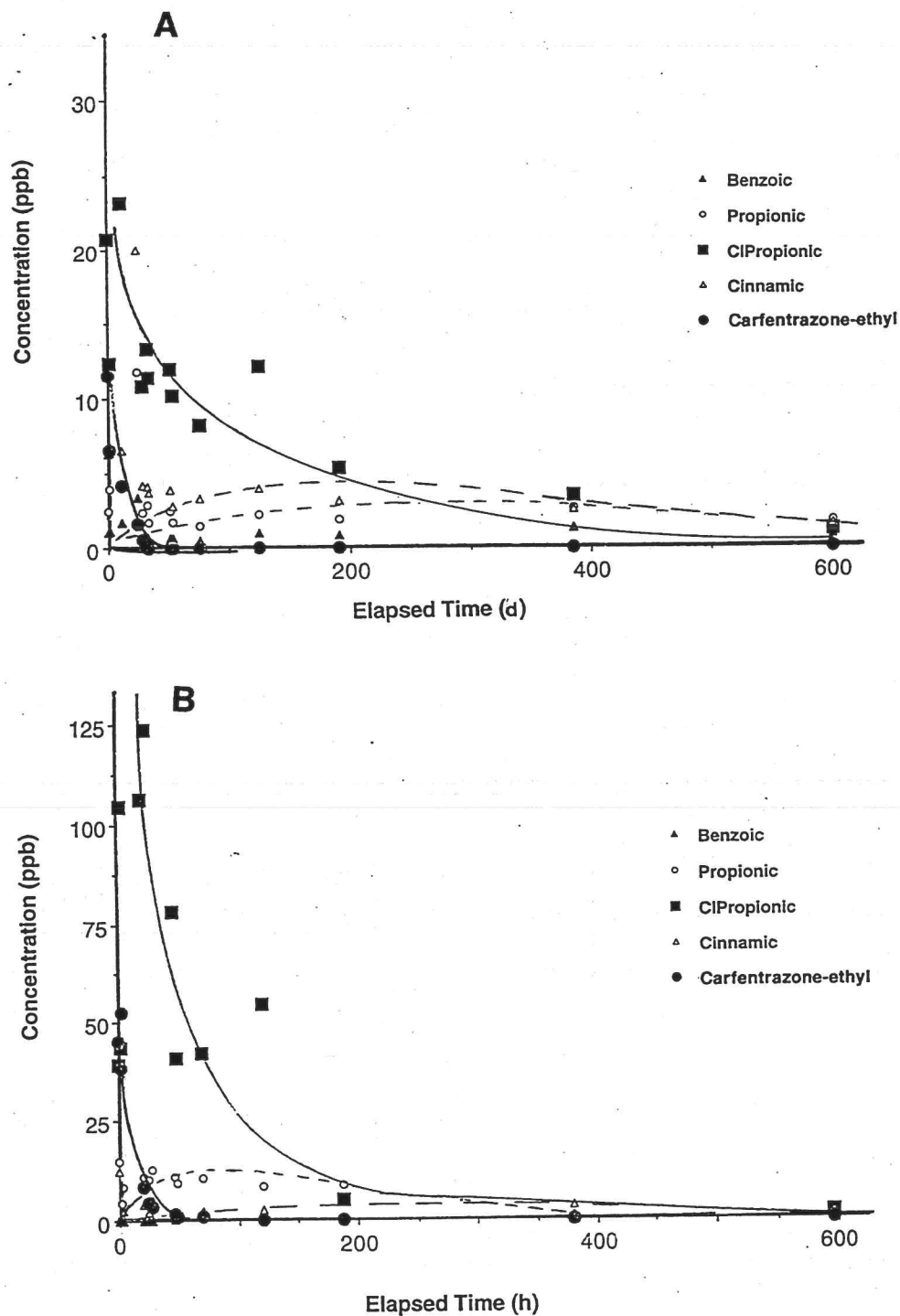


Figure 1. Dissipation of carfentrazone-ethyl in fieldwater at (A) Biggs (1.7 oz/acre preplant-incorporated) and (B) Richvale (3.2 oz/acre postflood). Acidified samples. Note difference in vertical scale.

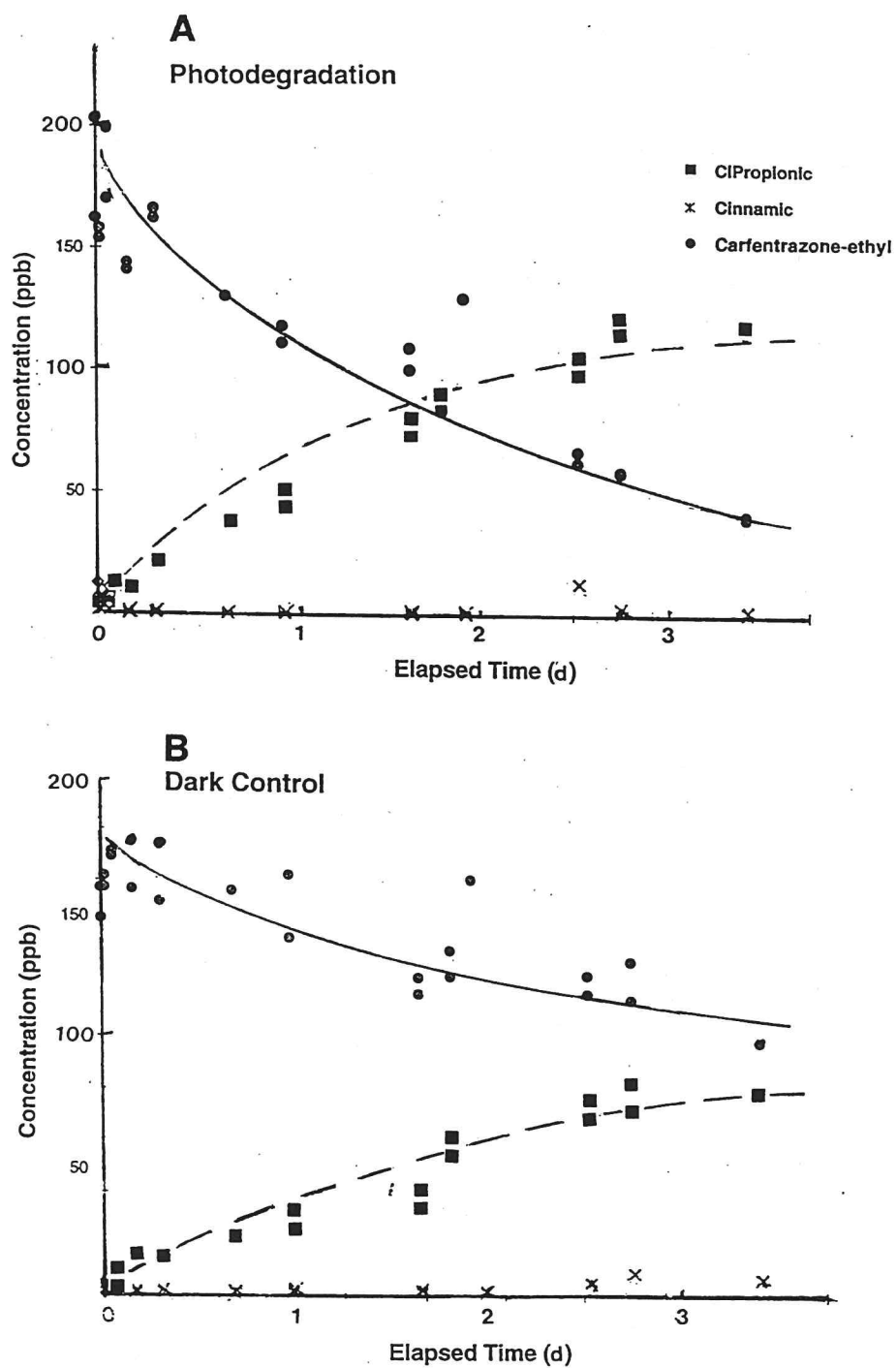


Figure 2. Laboratory degradation of carfentrazone-ethyl in UV light (A) and dark (B) in pH 7 buffer. Note difference in vertical scale.

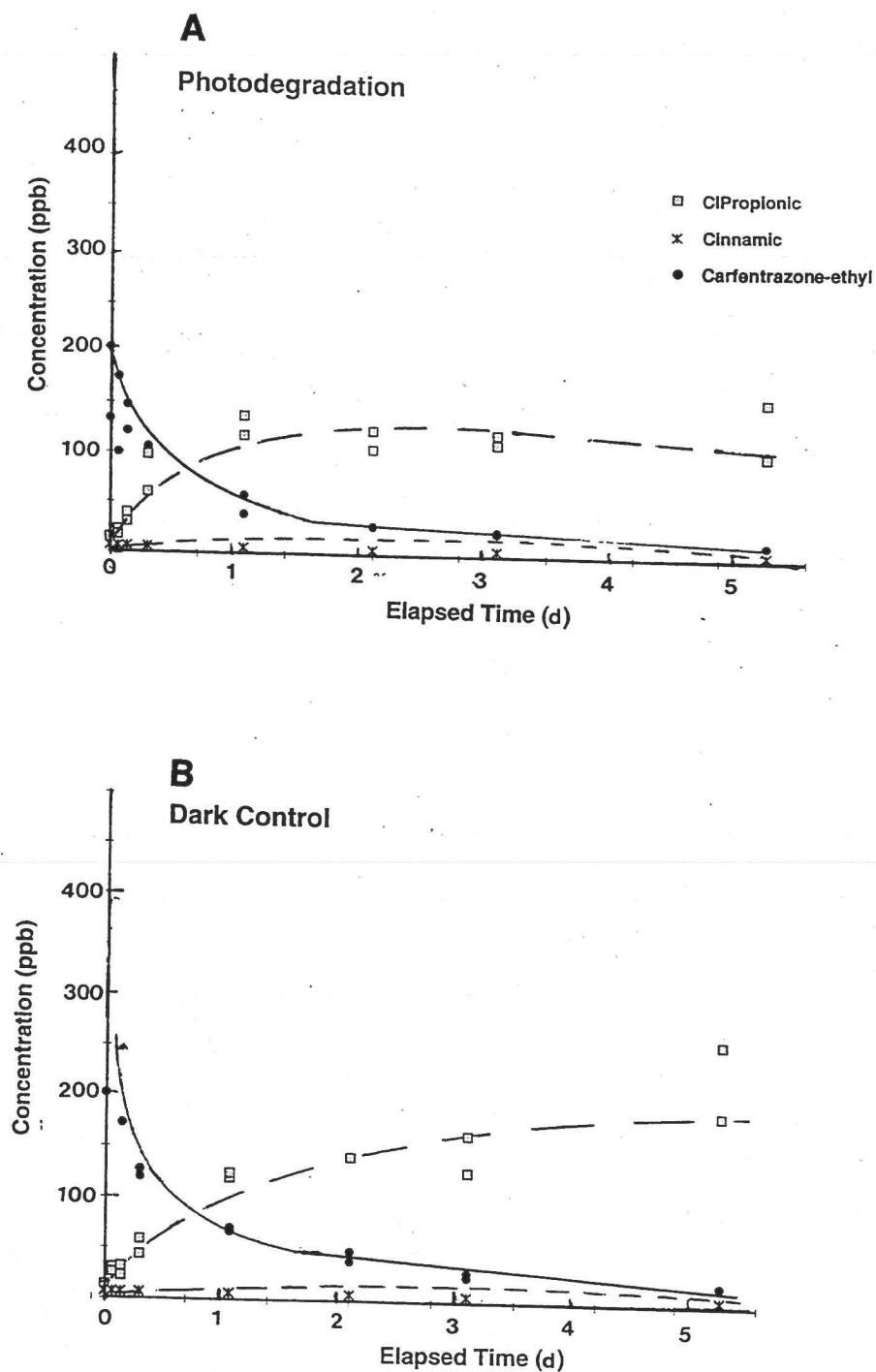


Figure 3. Laboratory degradation of carfentrazone-ethyl in UV light (A) and dark (B) in pH 7 field water.

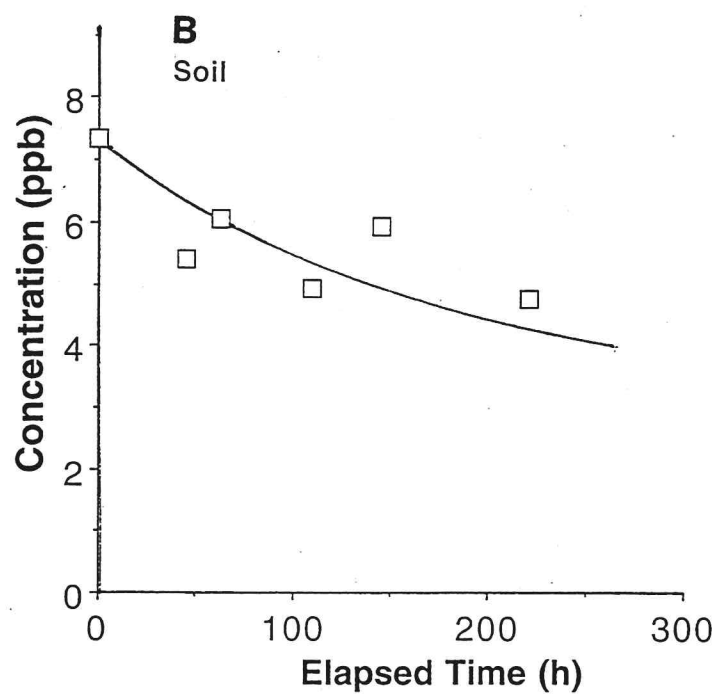
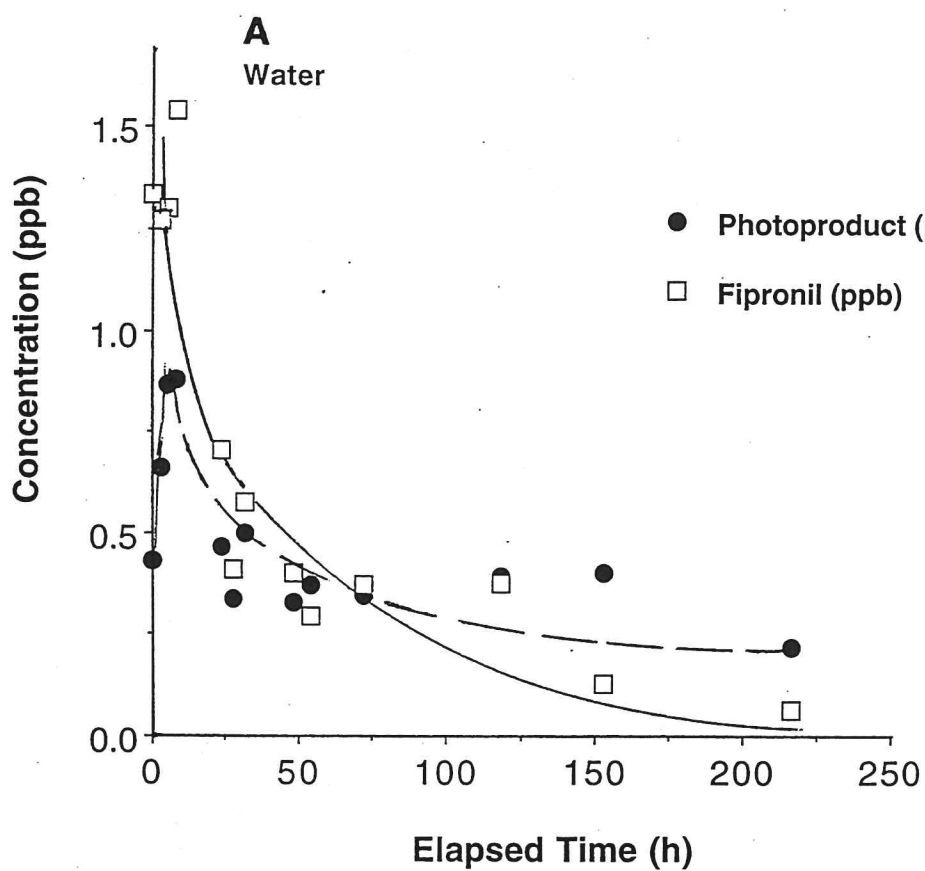


Figure 4. Field dissipation of fipronil in water (A) and submerged soil (B) at Richvale. Note difference in vertical scale.