

## Annual Report

### Comprehensive Research on Rice January 1, 1996 - December 31, 1996

**Project Title: The Environmental Fate of Pesticides Important to Rice Culture**

#### **Project Leader and Principal UC Investigators:**

Project Leader: D.G. Crosby, Environmental Toxicology Dept., UCD  
Principal Investigators: Ken Ngim and Dan Stewart, Environmental Toxicology Dept., UCD; Amy Witter, Facility for Advanced Instrumentation, UCD.  
Cooperators: Lance Beem (Rhône-Poulenc Ag Co.), Larry Godfrey (UCD Entomology Dept.), Jack Williams (Cooperative Extension, Sutter Co.)

**Level of 1996 Funding: \$37,220**

#### **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. Refine analytical procedures for fipronil and breakdown products (UCD).
2. Determine conditions for photoproduct formation (UCD).
3. Simulate fipronil breakdown in the laboratory (UCD).
4. Analyze of copper species in soil and water (UCD).
5. Measure the dissolution and mobility of copper species in soil (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 from water (UCD)
2. Determine the influence of formulation on fipronil persistence (UC-Davis and Biggs, Butte Co.).

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

1. Measure dissipation and breakdown of fipronil on a field scale (UCD and Sheridan, Placer Co.).
2. Search for a replacement for copper as an algicide (UCD).

#### **Summary of 1996 Research (Major Accomplishments) by Objective:**

##### **Objective I.**

**1. Fipronil Persistence.** Fipronil insecticide continues to be promising for the control of rice insects, including rice water weevils. However, it undergoes rapid photodegradation to a toxic product recently reported to be nondegradable in the environment, and so the US Environmental Protection Agency is expressing concern over the insecticide's projected use on paddy rice. The objective of this part of the research was to measure the formation and persistence of the photoproduct under laboratory conditions.

The very low application rates, which produce a maximum calculated concentration in field water of less than 20 ppb, has presented challenges for analytical measurements. However, our gas chromatographic method has been improved so as to allow quantitative analysis of fipronil and its principal breakdown products at levels down to 1 ppb in water and to a few ppb in soil.

Pure fipronil was dissolved in water at close to its maximum solubility in order to simplify subsequent extraction and analysis. Upon UV irradiation with aeration in a sunlight simulator, the insecticide dissipated with a half-life of 7 hrs, and photoproduct formed from the start (Fig. 1A). As the fractions of remaining fipronil and photoproduct did not add up to 1, air oxidation to other products was suspected and the experiment was repeated in the absence of air (under nitrogen). As shown in Fig. 1U, the rates of both fipronil degradation and photoproduct formation were similar to the aerated situation, although fipronil half-life increased by 32% to 10 hrs. Within the 70 hours (3 days) of each experiment, the photoproduct indeed appeared relatively stable, although it may have declined slightly in the presence of air. Oxidation apparently is not the only factor in photoproduct generation.

With pure photoproduct rather than fipronil, repeat experiments showed a half-life of 140 hrs when air was present, as opposed to 220 hrs in its absence (Fig. 2). However, the photoproduct certainly did dissipate, and only 6% remained at the end of 420 hrs (17.5 days). The compound was stable in the dark, but no other products were detected under UV irradiation. Field experiments (Objective 3) showed roughly similar results, but the laboratory experiments would be more meaningful under conditions closer to those existing in actual rice fields.

Further experiments were conducted in closed glass containers with fipronil dissolved in field water and irradiated with outdoor sunlight, and the results were compared to those of similar experiments with distilled water solutions. As shown by Fig. 3, fipronil degradation in distilled water was comparable to that in the lab reactor, while that in field water was somewhat slower and more comparable to what was seen in a rice field. The formation rate of photoproduct in field water also was similar to that in the field, while its formation in distilled water was markedly slower. Another experiment, this time with field water and soil, also gave results closer to those seen in treated rice fields (Fig 4). From this, it seems possible that a microcosm can be developed in which fipronil fate and persistence can be examined realistically in the laboratory.

**2. Copper mobilization and removal.** We previously reported on the relatively high levels of copper in rice fields treated repeatedly with copper sulfate ("bluestone"). With a view to mobilizing and potentially removing excess copper from the soil, experiments on the solubilization of highly insoluble copper sulfide, copper oxide, and copper hydroxycarbonate (malachite) showed the industrial natural products glycine (aminoacetic acid) and citric acid to be highly effective, while ammonia and other possible candidates were not. However, bringing these agents into the necessary intimate contact with rice soil proved difficult. Further, the chemical fate of copper sulfate in field water is much more complicated than it first appeared; polarographic measurements indicate that most of the copper is bound to natural organic matter in the water and soil so that little actually precipitates as insoluble malachite. Analysis of tailwater reveals that almost no copper leaves the field, so most must remain complexed with the soil.

## B. Objective II.

**1. Fipronil Volatility.** As shown in Fig.1, fipronil dissipates in water, but photodegradation does not account for all the loss. Volatilization seemed to be precluded, as fipronil's vapor pressure has been reported to be negligibly small ( $2.8 \times 10^{-9}$  torr). The Henry's law constant, which relates vapor pressure to water solubility and allows an estimate of a chemical's tendency to volatilize, was calculated to be  $3.38 \times 10^{-8}$  for fipronil and predicted that the insecticide should become more concentrated in water over time rather than evaporate.

The low solubility of fipronil precluded direct measurement of  $H'$  by standard methods; a novel experimental system was devised to measure it. The system performed well, and the measured  $H'$  of  $3.23 \times 10^{-2}$  shows that rather than being nonvolatile, fipronil can be expected to

volatilize quite rapidly from a flooded rice field (as we actually observe).

**2. The Influence of Formulation on Fipronil Persistence.** Several types of fipronil formulations have become available, and formulation properties often govern a pesticide's persistence. Fipronil persistence was measured in both the soil and water of 200 ft<sup>2</sup> field plots at the Rice Research Station at Biggs, CA, after application of either granular, dry flowable, or water-soluble formulations.

Figure 5 shows the insecticide's relative persistence in water. Fipronil from a granular formulation applied at the 3-leaf stage produced the highest concentration and persisted the longest, the dry flowable was next most persistent and produced more toxic photoproduct, while the soluble concentrate sprayed on soil pre-flood was least persistent and produced the least photoproduct. Fipronil from the granular formulation was still detectable after 400 hrs (17 days), and its photoproduct showed no sign of diminishing by the end of 300 hrs, while neither parent nor photoproduct were detectable in water past 150 hrs (6 days) when soluble concentrate was used.

In the corresponding soils, both the dry flowable and granular formulations resulted in very persistent residues (Fig. 6), while the soluble concentrate again was least persistent. Of the three, the soluble concentrate exhibits the most desirable properties.

### Objective III

**1. Field Persistence of Fipronil.** The water-soluble concentrate formulation was applied to one acre and 3-acre rice fields near Sheridan in Placer Co.. When the insecticide was sprayed on the soil just prior to flooding the 3-acre field, a relatively high peak residue of 5 ppb was produced in the water within 10 hrs but quickly dissipated (Fig. 7) and reached the limit of detection within less than 100 hrs (4 days). The photoproduct peaked at the same time but persisted at low levels out to the last sample time of 146 hrs (6 days). Data fluctuations at around 30 hrs may be due to sampling conditions. Soil residues of fipronil peaked quickly and then declined steadily (Fig. 8).

The one-acre plot was flooded, the water drawn down at the rice 3-leaf stage, and the soluble formulation applied. The maximum residue was only 20% of that seen after pre-flood application (Fig. 7), and it reached the detectability limit in water within about 60 hrs (2.5 days). The photoproduct approached undetectability within about 90 hrs. However, soil residues generally were higher and more persistent than those from a pre-flood application (Fig. 8).

**2. Alternatives to Copper as an Algicide.** Our previous reports have shown that almost all of the copper residues from annual applications of copper sulfate ("bluestone") for algae control remain on the treated fields. Limited attempts to remove the copper have not been successful, so toxic residues continue to accumulate. Examination of scientific literature has revealed recent work in Italy which suggests that the water-soluble and biodegradable aquatic herbicide, endothal, and its various salts may be worth reconsideration as a replacement for the copper (Maini, *Pesticide Science* **34**, 45-52 (1992)). Although endothal has been applied for weed control in California rice as recently as 1988, the amounts required risk toxicity to rice plants. Levels used for algae control appear to be lower.

### Publications and Reports

1. Gever, J.R., S.A. Mabury, and D.G. Crosby. 1996. Rice field surface microlayers: Collection, composition, and pesticide enrichment. *Environ. Toxicol. Chem.* **15**: 1676-1682.
2. Mabury, S.A., J.S. Cox, and D.G. Crosby. 1996. Environmental fate of rice pesticides in California. *Reviews Environ. Contam. Toxicol.* **147**:71-117.
3. Mabury, S.A., and D.G. Crosby. 1996. Pesticide reactivity toward hydroxyl and its relationship to field persistence. *J. Agr. Food Chem.* **44**: 1920-1924.

## Concise General Summary of Current Year's Results

1. Reports of the high environmental stability of the toxic photodegradation product of the promising rice insecticide, fipronil, are erroneous. The photoproduct is persistent but degradable, with a half-life of 135 hrs (5.6 days) under controlled laboratory conditions and as short as one day in the field, depending on formulation and conditions. This observation may substantially assist registration of fipronil for use on rice.

2. Simulation of fipronil field dissipation under controlled conditions in a laboratory microcosm containing field water and soil appears possible. This would allow more rapid evaluation of methods for controlling photoproduct formation.

3. Contrary to the nonvolatility reported in the literature, a significant part of fipronil loss from flooded rice fields appears to be due to volatilization. This information should assist registration of fipronil for use on rice.

4. Comparison of fipronil persistence resulting from application of granular, dry flowable, or water-soluble formulations to field plots indicates that the soluble form is superior to the others.

5. Field-scale application of fipronil as a water-soluble formulation at the rice 3-leaf stage resulted in a half-life of 24 hrs in water, with residues no longer detectable within only 2.5 days. This is very favorable.

6. Attempts to mobilize or remove copper from bluestone-treated soil were largely unsuccessful, and the fate of the copper in field water proved to be more complicated than it first appeared.

7. The old aquatic herbicide, endothal, may be worth reconsidering as a possible replacement for copper sulfate ("bluestone") for algae control in flooded rice. The amine salt formulation, especially, is nonpersistent in soil and water and shows only limited toxicity to fish and aquatic invertebrates.

  
Project Leader

10 December 1996  
Date

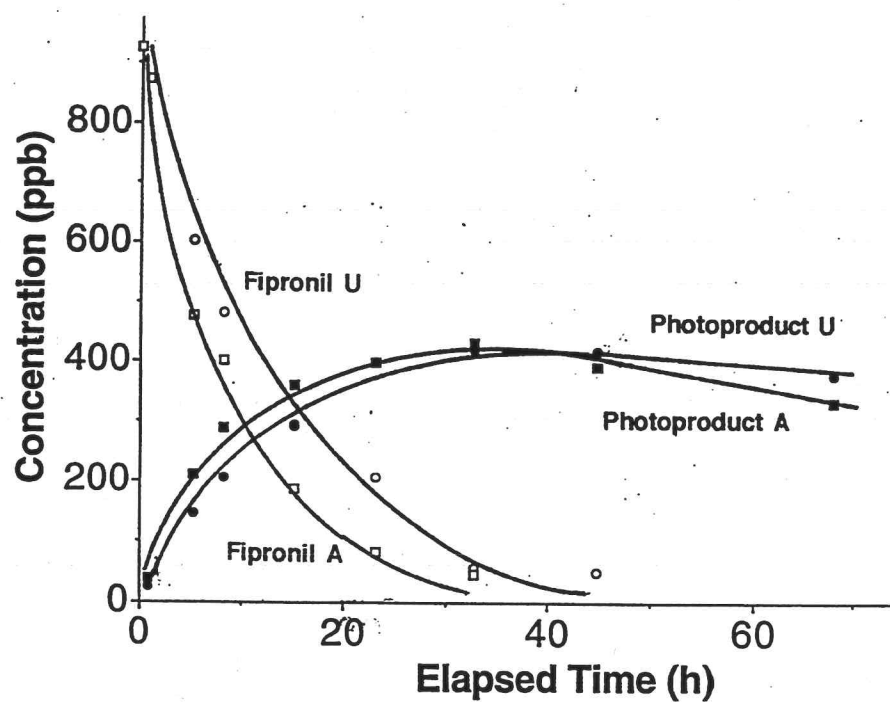


Fig. 1. Fipronil dissipation in a laboratory photoreactor, (A) aerated or (U) unaerated.

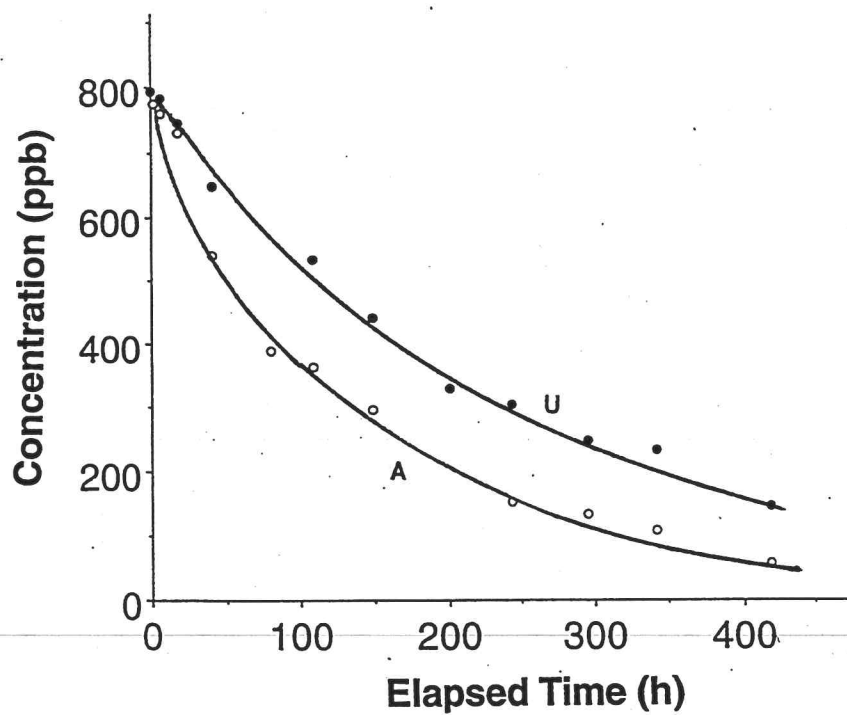


Fig. 2. Photoproduct dissipation in the photoreactor, (A) aerated or (U) unaerated.

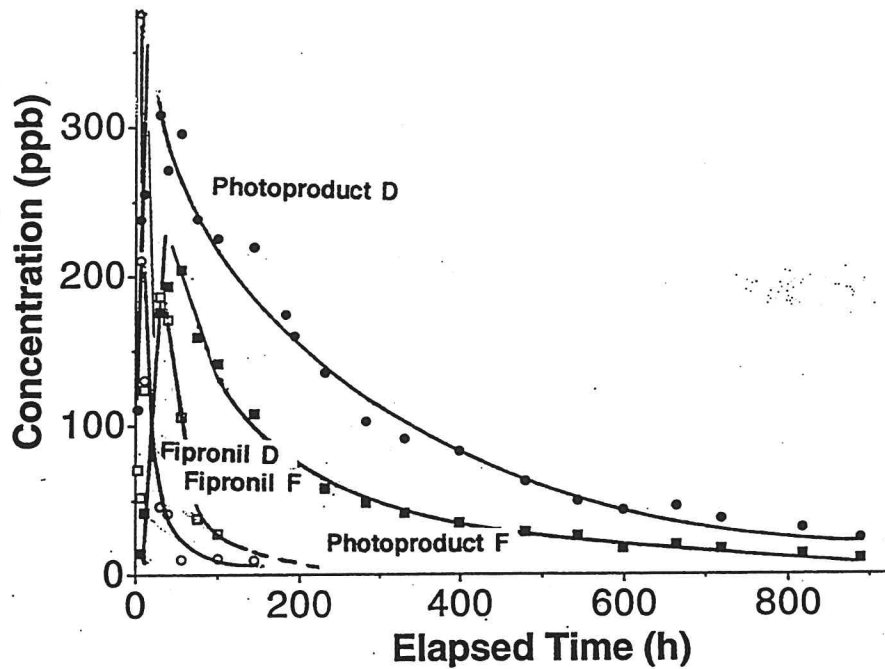


Fig. 3. Fipronil dissipation in a closed sunlit reactor in (D) distilled water or (F) field water.

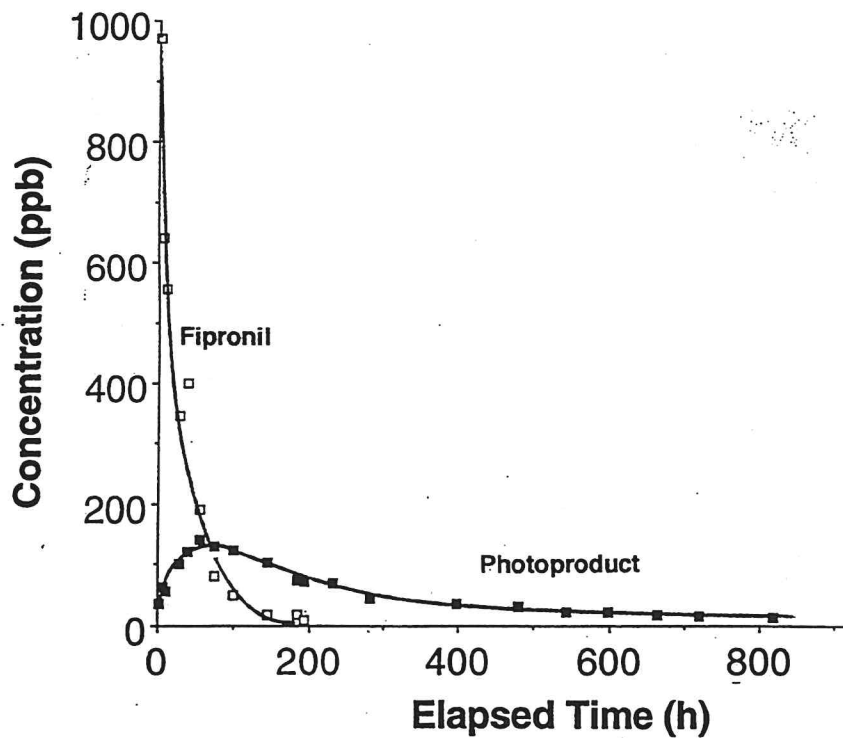


Fig. 4. Fipronil dissipation in a closed sunlit reactor containing field water and rice soil.

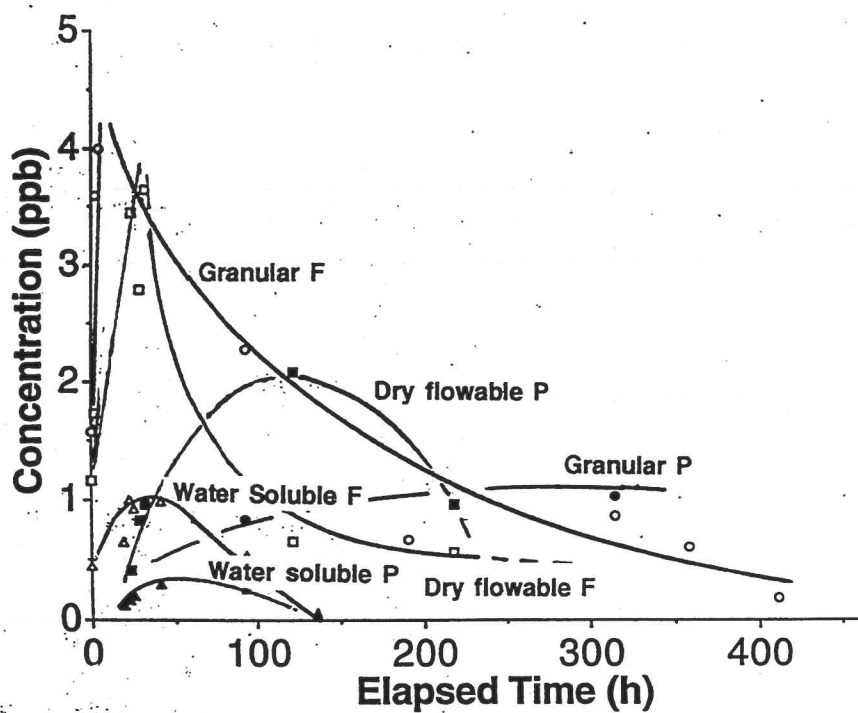


Fig. 5. Fipronil (F) and photoproduct (P) residues in water, 200 ft<sup>2</sup> field plots.

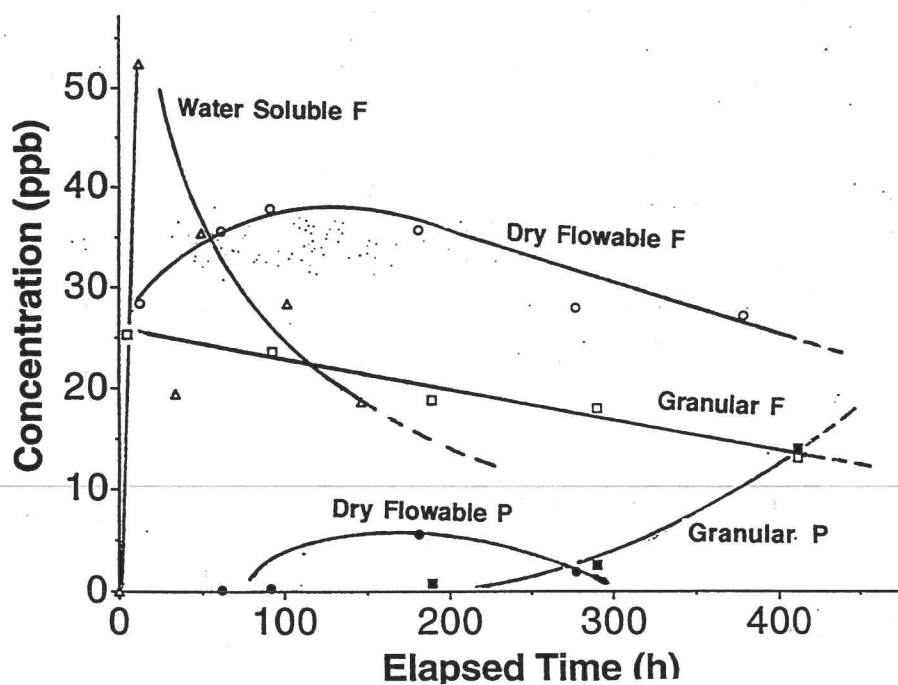


Fig. 6. Fipronil (F) and degradation product (P) residues in soil as in Fig. 5.



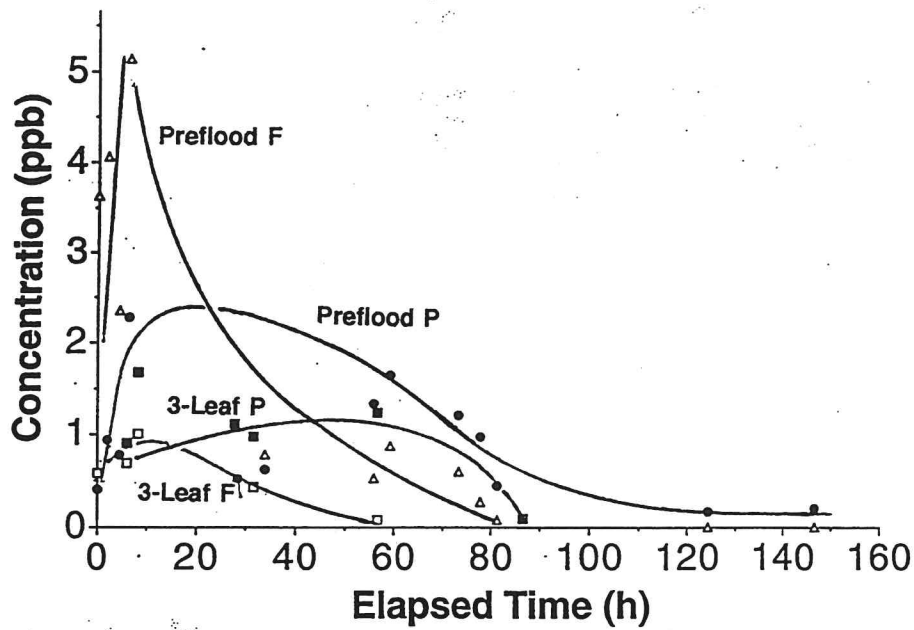


Fig. 7. Fipronil (F) and photoproduct (P) residues in water on 1- and 3-acre fields, sol. concentrate preflood or at 3-leaf stage.

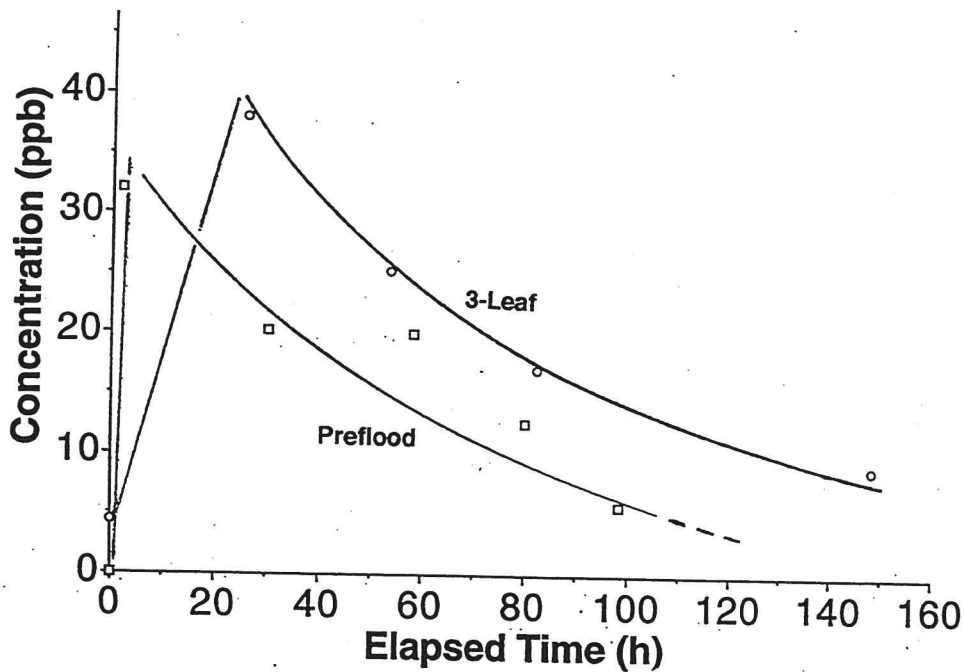


Fig. 8. Fipronil residues in soil as in Fig. 7.