

Comprehensive Research on Rice Annual Report

January 1, 1994 – December 31, 1994

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

Project Leader and Principle UC Investigators:

Project Leader: D.G. Crosby, Environmental Toxicology Dept., UC-Davis.

Principle Investigators:

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Cooperators:

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Level of 1994 Funding: \$52,604

Objectives and Experiments Conducted by Location to Accomplish Objectives:

- A. Objective I.** To identify, investigate, and model environmental factors which govern movement and chemical fate of rice pesticides.
1. Analytical method development for carbonate radical (UCD).
 2. Measurement of carbonate radical in field water (UCD).
 3. Reactions of carbonate radical (UC).
 4. Copper Mobilization (UCD).
- B. Objective II.** To estimate the relative importance of such factors to the practical use of specific rice pesticides.
1. Survey of copper in soils (UCD and Sills Ranch, Sutter Co.).
 2. Distribution of copper in soil and water (UCD and Sills Ranch, Sutter Co.).
 3. Copper toxicity to rice (UCD and Rice Reserch Station, Biggs).
 4. Deschlorothiobencarb sampling and analysis (UCD and Sutter Co.).
 5. Thiobencarb degradation experiments (UCD).

- C. **Objective III.** To apply research results toward meeting regulatory requirements and improved management of rice pesticides.
1. Fipronil analytical method development (UCD).
 2. Fipronil photodegradation (UCD).
 3. Pesticide mobility in soils (UCD).

Summary of 1994 Research (Major Accomplishments) By Objective:

A. Objective I.

1. Pesticide Persistence: Influence of Carbonate and Hydroxyl Radicals

Development of a highly sensitive and selective method was completed for measurement of carbonate radicals generated in water by reaction of natural hydroxyl radical with dissolved carbonate or bicarbonate ("hardness"). Measurements in 15 different field waters showed a relatively consistent, steady-state concentration of 10^{-14} M, depending upon hydroxyl production rate, alkalinity, and dissolved organic matter. While this level may seem very low, it afforded desulfurization of the organophosphate insecticides fenthion, methyl parathion, and chlorpyrifos, oxidation of the herbicide thiobencarb, and reaction with several other test compounds. However, the unknown generation rate of hydroxyl, a key step, precluded quantitative rate measurements; a new method for hydroxyl generation from potassium peroxyxynitrate will now permit them to be made.

2. Copper Mobilization

The relatively high levels of copper found in some rice fields, and the annual addition of more, may inadvertently become mobilized by nitrogen fertilizers and other substances; such mobilization also might be adapted to reduce the copper levels necessary. Newly precipitated copper enters field soil primarily as cupric hydroxycarbonate (malachite) and later may be converted naturally to cupric oxide and sulfide.

Freshly-prepared cupric hydroxycarbonate was treated with aqueous solutions containing an excess of each of several complexing agents which are fertilizers or natural products. Ammonia and glycine almost immediately dissolved the copper compound; Ammonium sulfate, ammonium carbonate, and ethanolamine were slower, and urea caused no effect. Next, a low-copper soil was fortified with cupric hydroxycarbonate at 100 ppm, aliquots were shaken with the various solutions, and the dissolved copper analyzed spectrophotometrically. Soil columns proved unsatisfactory due to slow drainage; the quantitative trial gave ambiguous results and will be repeated, but the qualitative test showed that the highly insoluble copper compounds are capable of mobilization.

B. Objective II.

1. Copper in California Rice Fields

Copper sulfate pentahydrate ("bluestone") was applied by aircraft to 20 field basins of about 0.4 acres each at the standard rate of 10 lbs/acre for control of algae and tadpole shrimp. Six basins were sampled to measure the dissipation of copper (Cu) from the water, three for uptake of copper by sediment, and one was intensively monitored for copper in soil, field water, and released tailwater. Cu analysis in water were conducted spectrophotometrically in our laboratory and those in soil by the DANR laboratory at UCD.

The initial loss of copper from water was rapid (Fig.1); the concentration dropped by half within 12 hours. The loss slowed after about 24 hours, and low levels were still detectable even after 320 hours (13 days). The difference from our 1993 results (half-life 4 hours) may be due changes in pH and soil type. The dissolved copper was not present as cupric ion but was apparently bound to soluble organic matter. Had all of the applied bluestone dissolved, as is required for control of algae and tadpole shrimp, the initial concentration would have been about 11.6 ppm (2.95 ppm Cu); the maximum initial Cu content actually was about 0.3 ppm, showing that only 10% of the bluestone was in solution where it could be effective.

While only about 50 grams of total copper was found initially in the water of each basin, the first time point (15 minutes) showed over 500 g. in the top 2 mm of sediment, partly as precipitated hydroxycarbonate and partly in soil-bound form (Fig.2). Subsequently, the level appeared to decline slowly with time, due partly to downward movement in the sediment and perhaps partly to resuspension in the water column. Over the first 48 hours, no more than 1.2 g. of Cu (0.26%) left the basin in tailwater.

The 1994 survey of rice soils in Colusa, Glenn, and Sutter counties (Table I) showed an overall average Cu content of 51 ppm compared to 32 ppm in untreated soil (Sacramento National Wildlife Refuge), with a single high value of 301 ppm. The bioavailable fraction averaged 10.3 ppm. However, as 10 lbs/yr of added bluestone should increase the Cu content in the disk zone of rice soil by about 3 ppm per year, and bluestone application has been going on for decades, some unforeseen loss mechanisms may operate, for example a combination of plant uptake, deeper migration, and mobilization.

Table I. Copper levels in some California rice soils, 1994

Sutter Co.		Glenn Co.		Colusa Co.	
Bioavailable (ppm)	Total (ppm)	Bioavailable (ppm)	Total (ppm)	Bioavailable (ppm)	Total (ppm)
4.0	15	4.2 ^a	32 ^a	6.9	49
3.9	17	4.1	66	9.8	74
5.1	26	76.8	301	7.7	53
7.1	35	14.8	84	11.1	65
6.1	24	8.6	57	10.8	61
5.4	23	13.7	70	10.2	67
7.6	36	11.1	54	<u>13.6</u>	<u>72</u>
5.4	46	9.6	46	avg 10.0	avg 63
9.8	54	13.9	64		
<u>10.4</u>	<u>54</u>	9.0	51		
avg 6.5	avg 33	10.1	58		
		4.8	42		
		9.1	49		
		15.4	64		
		11.2	68		
		<u>4.9</u>	<u>47</u>		
		avg 14.5	avg 57 ^b		

^a Sacramento National Wildlife Refuge

^b Avg. without 301 ppm.

Initial greenhouse and field experiments were conducted to determine the effects of soil copper levels on rice plants. In the greenhouse, flooded soil contained 50, 100, 250, and 550 ppm of Cu. At 150 and 250 ppm, the plants were visibly stunted, while those at 550 ppm were heavily impacted; chlorophyll loss mirrored these effects (Fig. 3). Duplicate field plots in 6-ft. diameter rings set in a rice field at the Biggs station contained Cu at 50, 250, 500, and 700 ppm – far higher than planned. Although the plots showed a visual gradation in color, height, and stand during growth, and corresponding stunting of roots, grain yields were not as severely reduced as had been expected (Fig. 4) except in the highest treatment.

2. Deschlorothiobencarb (DCT)

DCT, a microbial degradation product of thiobencarb (Bolero®), has been reported to cause phytotoxicity in thiobencarb-treated rice fields in Japan. This damage is now being observed in some California rice fields. Soil samples were collected from two separate fields in which damage was apparent, and control soils from each field were collected in areas that had suffered no visible damage. The samples were air-dried, solvent-extracted, and the extracts analyzed by a very sensitive gas chromatographic method described in our 1993 Report. As shown in Fig. 5, all samples contained both thiobencarb (TB) and DCT, but soil from the damaged areas always contained DCT at greater than 0.5 ppm. The phytotoxicity of DCT appears to be real.

Samples of the active soil were placed in glass containers, the soil surfaces covered with water, treated with TB to bring concentrations to 5 ppm, and incubated at room temperature; these were then processed at intervals and analyzed. Fig. 6 shows that as TB was degraded, DCT levels increased. The 28-day soil sample was air-dried to make it aerobic, after which DCT levels were seen to drop off. We interpret this to mean that DCT is formed readily from TB under anaerobic conditions but is itself biodegraded under aerobic conditions. The experiments are being repeated with sterilized soil to assure that the effect is due to biodegradation rather than purely chemical degradation.

C. Objective III.

1. Fipronil® Analysis by ¹⁹F NMR Spectrometry

Fipronil® and Dimilin® (diflubenzuron) are fluorine-containing insecticides. Our 1993 Report described a trial analysis of diflubenzuron by a new fluorine-specific method called ¹⁹F NMR spectrometry. As Fipronil® presently looks promising for applications in rice and is also much more water-soluble than is diflubenzuron, a ¹⁹F NMR method was developed for its analysis and then applied in an initial laboratory test of Fipronil photodegradation in water. The parent compound showed two distinct peaks representing the two different locations of CF₃ groups (Fig. 7); it underwent rapid photodegradation when the sample tube was exposed to sunlight, and the stepwise formation of many (as yet unidentified) breakdown products was easily seen. This work will be expanded in 1995.

2. Pesticide Mobility in Soils

The mobility of pesticides in soil has been determined in several ways, including analyzing fractions collected from large soil columns and thin-layer chromatography of radiolabelled compounds on soil plates. We successfully applied small-diameter soil columns with continuous monitoring of effluent by wavelength-specific UV detector used for high-pressure liquid chromatography (HPLC). The method also permits the mobility measurements with pesticide mixtures. Unfortunately, the transfer of investigator Jerry Ito out of our research group precluded completion on this project.

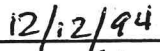
Publications and Reports

- S.A. Mabury. *Hydroxyl Radical in Natural Waters*, PhD Thesis, UC-Davis, December 1993.
- S.A. Mabury and D.G. Crosby. The use of fluorine NMR for agrichemical research. *Abstr. VIII International Congress of Pesticide Chemistry*, Washington, D.C., July 1994.
- D.G. Crosby. The fate of diflubenuron in rice fields. *Report to USDA Regional Research Project W-45*, Reno NV, May 1994.

Concise General Summary of Current Year's Results

1. The powerful oxidizing agent, hydroxyl radical, generated by sunlight in field water, is rapidly converted to another oxidant, carbonate radical, by reaction with dissolved carbonate and bicarbonate minerals. The carbonate radicals then can take part in the degradation of many pesticides.
2. A repeat of our 1993 aerial application of copper sulfate (bluestone) to rice plots for control of algae and tadpole shrimp again showed that very little copper stays in the water column -- often not enough for effective action -- and that almost all resides in the sediment within about 15 minutes after application. Almost none appears to leave the field in tailwater.
3. Analysis of soil samples from 32 rice fields in Colusa, Glenn, and Sutter counties for total and bioavailable copper showed totals ranging from 3.9 ppm to 301 ppm, with an average of 50 ppm. Each application of bluestone 10 lbs/acre theoretically increases soil copper by 3 ppm.
4. Greenhouse and field tests of the effect of soil copper on rice plants showed that phytotoxicity appeared at 150 ppm Cu and became progressively more severe up to almost complete lethality at 700 ppm. Surprisingly, rice yields were reduced only 10% at 250 ppm and 20% at 500 ppm, suggesting that most rice soils are a long way from harmful copper levels.
5. At present the phytotoxicity of the thiobencarb (Bolero®) degradation product, deschlorothiobencarb (DCT), to rice appears real, and the concern is that it could spread. DCT is formed under flooded (anaerobic) conditions and degraded when the soil is exposed to air, suggesting that extended flooded may not be advisable for some fields.


 Project Leader


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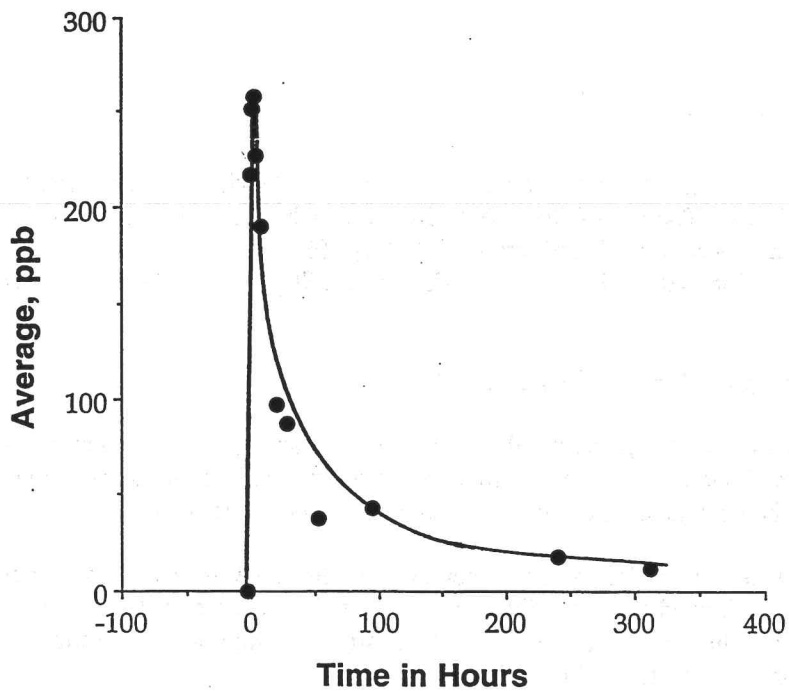


Fig. 1. Rate of loss of dissolved copper from field water.

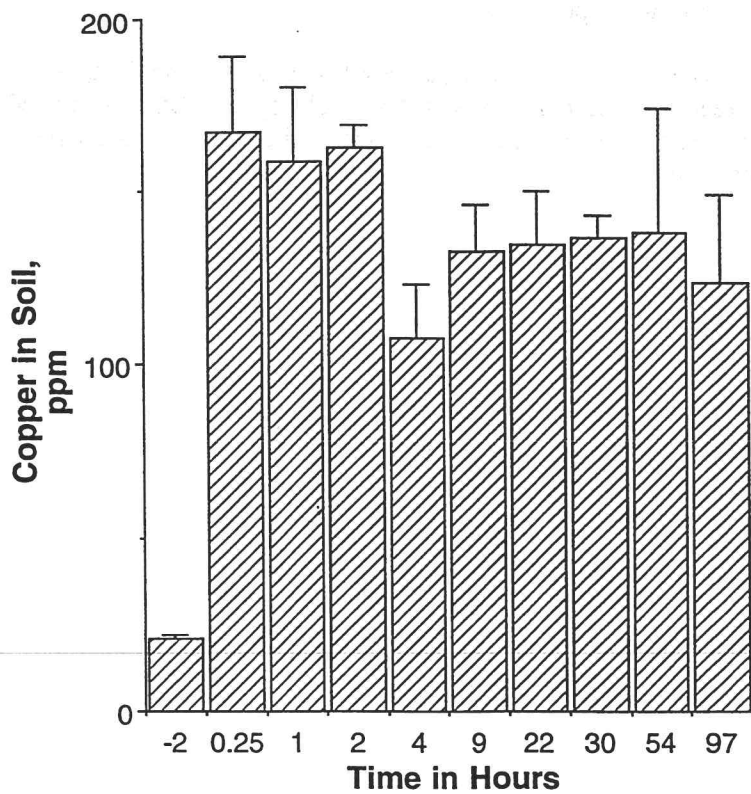


Fig. 2. Rate of copper deposition in the top 2 mm of sediment.

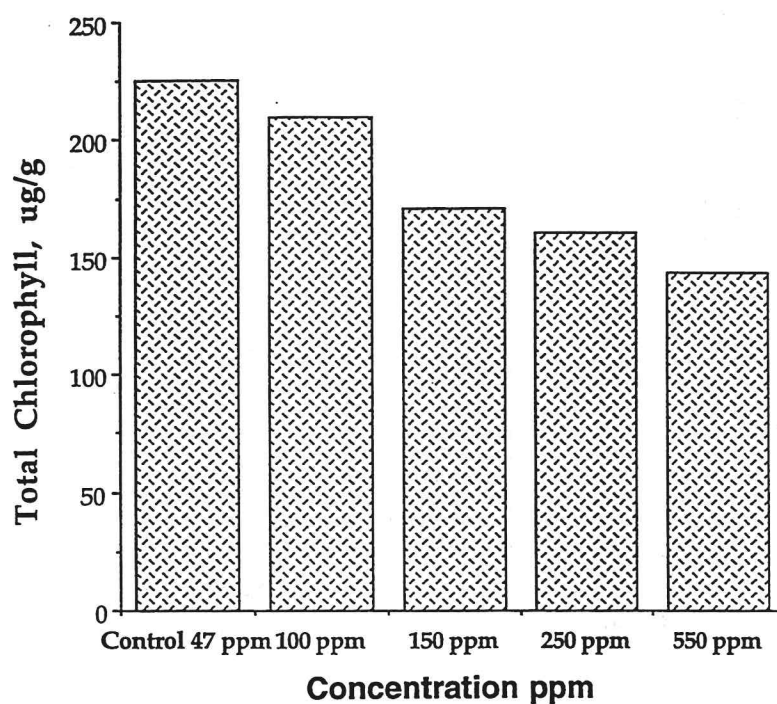


Fig. 3. Chlorophyll content of copper-treated rice plants.

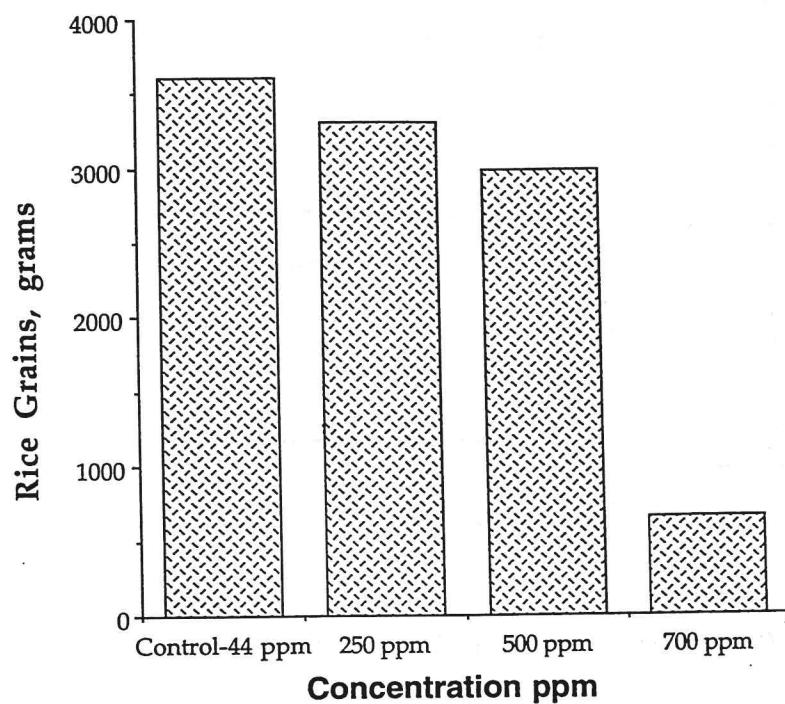


Fig. 4. Rice yields from copper-treated field plots.

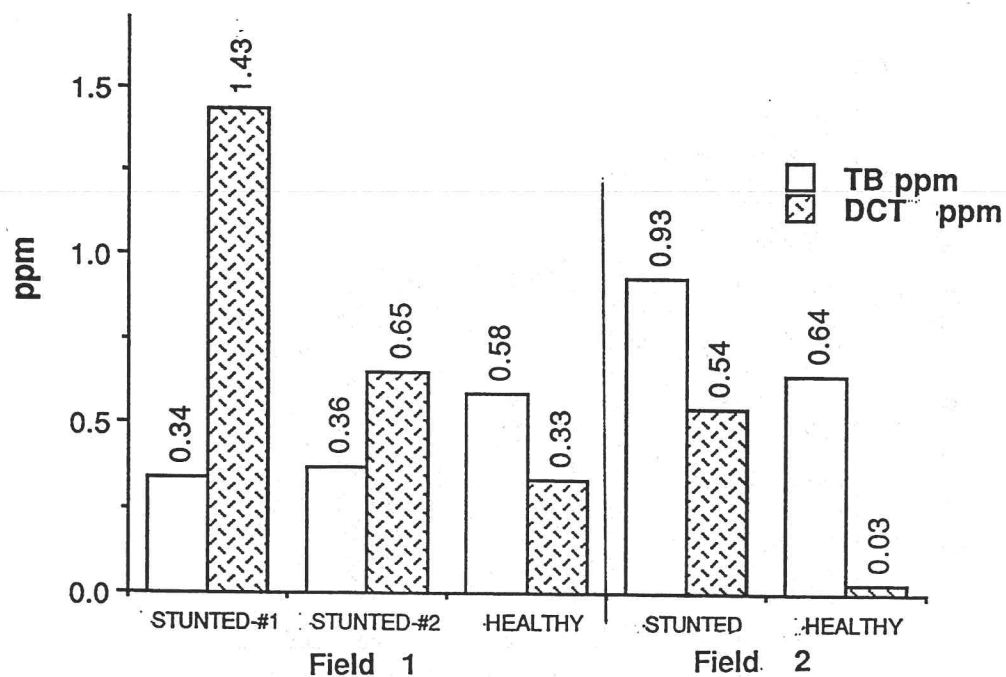


Fig. 5. Thiobencarb (TB) and deschlorothiobencarb (DCT) in field soils.

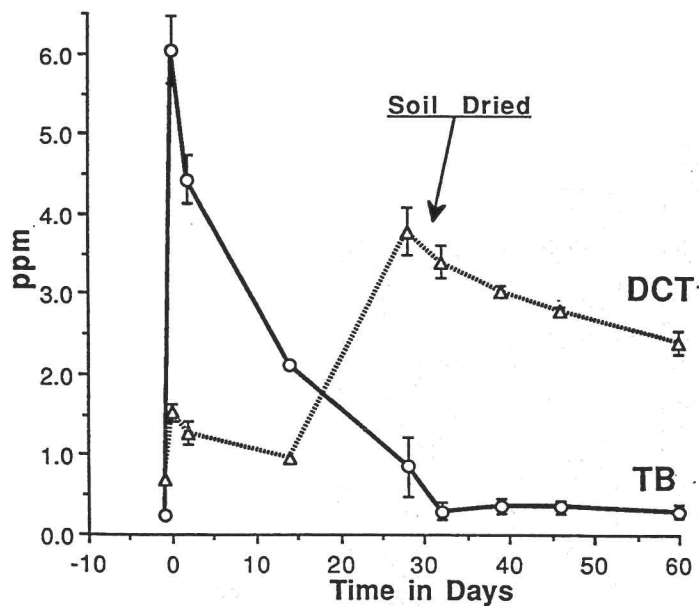


Fig. 6. Degradation of TB and DCT in active soils.

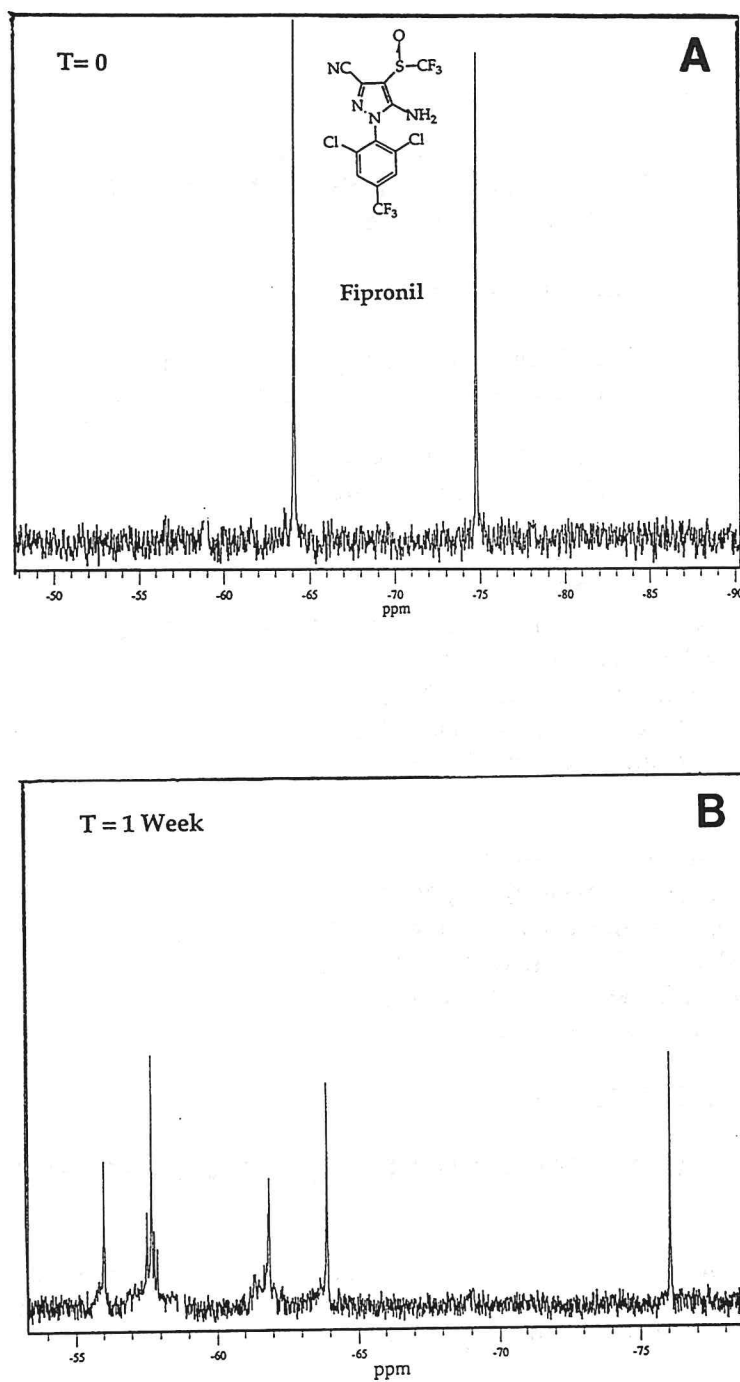


Fig. 7. ^{19}F NMR analysis of Fipronil (A) and its photodegradation products (B) in water.