

**COMPREHENSIVE RESEARCH ON RICE
ANNUAL REPORT**

January 1, 1987 - December 31, 1987

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

PROJECT LEADER AND PRINCIPLE UC INVESTIGATORS:

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We regret to report the death of J.B. Bowers on October 29, 1987. He had been a major investigator on this project since its inception, 11 years ago.

LEVEL OF 1987 FUNDING: \$39,470 (including carryover).

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. Photodegradation of bentazon (Basagran®) in the laboratory microcosm and the field (UCD; Rice Research Facility).
 2. Zinc oxide-catalyzed photooxidation of bentazon in water (UCD).
 3. Bentazon movement in Sacramento Valley soil (UCD).
 4. Photodegradation of Londax® in water (UCD; CSU-Chico).
 5. Analytical determination of quinclorac (BAS 514H) UCD).
 6. Environmental properties of quinclorac (UCD).

- B. Objective II.** To estimate the relative importance of such factors to the practical use of specific rice pesticides.
1. Reabsorption of molinate and thiobencarb into water (UCD; Elkhorn, Yolo Co.).
 2. Field dissipation of Londax (Rehermann Ranch, Butte Co.; CSU-Chico).
 3. Field dissipation of quinclorac (Biggs, Butte Co.; UCD).
- C. Objective III.** To apply research results toward meeting regulatory requirements and improved management of rice pesticides.
1. Persistence of thiobencarb (Bolero®) in recirculating field water (UCD; Mace Ranch, Sacramento Co.).
 2. Photodegradation of MCPA spray residues in the presence of bleach (UCD).
 3. Zinc oxide-catalyzed photodegradation of bentazon (Basagran®) in treated fields (UCD; Scheidel Ranch, Sutter Co.).

SUMMARY OF 1986 RESEARCH (MAJOR ACCOMPLISHMENTS) BY OBJECTIVE:

A. Objective I.

1. Environmental degradation of bentazon (Basagran®).

Dissipation rates of bentazon have been discussed in our previous Annual Reports. Field dissipation curves clearly showed that sunlight was the major factor in the loss of its residues from water, and so the identification and persistence of the photodegradation products assumed particular importance.

Even idealized photodegradation experiments in pure water produced complex mixtures of products (Fig. 1A), but removal of most of the unreacted bentazon (I) by crystallization (Fig. 1B) or chromatography (Fig. 1C) made possible the eventual isolation of the principal products II, III, and IV and analysis of 8 others. By comparison, bentazon solution held in the dark slowly generated one major product (II) and several minor ones (a,c,d,g) which persisted.

Compounds II, III, and IV were examined by several sophisticated techniques of mass spectrometry and nuclear magnetic resonance (NMR) spectrometry, a very difficult and time-consuming process. The results provided the chemical structures proposed in Fig. 2; none of these substances have been reported previously in the literature. Compounds V and VI have been reported before as products of bentazon photodegradation but were not observed in our experiments, perhaps because they may be formed only slowly and in small amounts under our conditions, and VI is known to be rapidly photodegraded itself.

The rate of formation and disappearance of the major products and a few of the minor ones in the microcosm is shown in Fig. 3; as authentic specimens of these materials were not available, elapsed time has been plotted against ultraviolet (UV) detector response which indicates concentrations in the low ppb range. Compound II was formed in the dark by hydrolysis, but, like photoproduct IV, it was degraded by

further exposure to light. However, of particular interest were those minor products (a,c,d,f) whose concentration continued to increase even in the dark, as well as the photoproducts IV, e, and h which likewise were stable in light (Fig. 3). Similar results also were observed in field measurements made at the UCD Rice Research Facility (Fig. 4), although there the concentrations of major products II and IV were observed to keep increasing over the 50-hour experiment.

Whether in the field or microcosm, the half-life of bentazon was on the order of 3-6 days (Table I), and sunlight UV was essential for dissipation (Experiments II and III). However, some of the photodegradation products persisted for at least a week, and their toxic implications and final fate still remain unknown. Photo-oxidation catalyzed by zinc oxide proceeded smoothly to give a bentazon half-life of about 40 minutes, but degradation appeared to be extensive and none of the above photoproducts were detected.

Table I. Field Study and Microcosm Experiments with Bentazon

Experiment	Water	Profiles	
		UV	Half-life (days)
I field study	ricefield	field	2.90
II microcosm	distilled	none	65.10
III microcosm	ricefield	none	30.30
IV microcosm	distilled	constant	3.00 ± 0.13
V microcosm	distilled	constant	4.12 ± 0.10
VI microcosm	ricefield	constant	3.32 ± 0.22
VII microcosm	distilled	diurnal	6.39 ± 0.24
VIII microcosm	ricefield	diurnal	4.45 ± 0.37

2. Environmental persistence of Londax.

In previous Annual Reports, we discussed the slow photodegradation of Londax in water under sunlight or indoor UV radiation (half-life greater than 30 days). As data released to us by the manufacturer (E.I. duPont) indicated a laboratory photolysis half-life of 4 hours, representing low persistence, it was necessary to explain the discrepancy. The duPont experiments for product registration were conducted with a fluorescent "black-light" UV source which inadvertently provided some high-energy UV, and a photoreactor bearing a UV-transmitting quartz window. The Londax was dissolved in water containing acetone, which initiates certain kinds of photochemical reactions.

Use of a quartz container and UV source (Sylvania 350 BL) similar to duPont's (Table II) caused rapid photodegradation which was accelerated by acetone; no reaction occurred under sunlight in the absence of acetone. Londax must be considered as environmentally unreactive.

Table II. Photodegradation of Londax

Conditions	% Degradation in 5 Hrs.		
	Low-energy Lamps ^a	High-energy Lamps ^b	Sunlight ^c
Pyrex, dist'd water	0	0	0
Pyrex, aqueous acetone	-	45	15
Quartz, dist'd water	0	53	0
Quartz, aqueous acetone	-	99	12

^aSylvania 350BL. ^bWestinghouse FS40. ^cJune 1987.

3. Environmental properties of quinclorac (BAS 514H).

In order to determine the important environmental properties of quinclorac, it was necessary to develop sensitive methods for analysis of water and soil at the part-per-billion (ppb) level. Quinclorac was removed from water satisfactorily by nonionic resins; gas chromatography of the resulting concentrate after derivatization gave 90-100% recovery and 1 ppb sensitivity. Liquid chromatography (HPLC) with 90-100% recovery was sensitive to 5 ppb, but field water samples could be analyzed directly without extraction or derivatization.

Quinclorac was stable toward sunlight in distilled water but was slowly degraded in filter-sterilized rice-field water (Fig. 5). In unsterilized field water in the laboratory photoreactor, it was degraded at about the same rate in both dark and light (10% loss in 30 days), suggesting the slow breakdown by microorganisms. The principal photodegradation product was identified as 3,7-dichloroquinoline and occurred together with 3 unidentified minor products. Determination of the Henry's Law constant indicated that quinclorac does not volatilize from water and so may be concentrated as water evaporates. At pH 8, it was not appreciably bound to rice-field sediment (sandy loam).

In the presence of low (100 μ M) levels of added hydrogen peroxide, the photolysis rate of quinclorac was greatly increased in field water (30% degradation in 10 days), indicating that its degradation in a rice field would be dependent upon the concentration of natural photo-oxidant present at application time. Other routes of loss appear to be relatively unimportant.

B. Objective II.

1. Reabsorption of molinate and thiobencarb.

Our previous reports have shown that volatilized molinate and thiobencarb could be reabsorbed into clean water at the field application site. Could reabsorption of vapor be a source of residues in Sacramento River water?

Containers of distilled water were set up in the river near Elkhorn (Yolo County) and monitored during the several days of peak 1987 herbicide application. Although the odor of molinate could be detected in the area, no herbicide residues were found down to the limit of analytical detectability (<1 ppb). We conclude that reabsorption from the atmosphere is not a significant source of herbicide residues in the river.

2. Field dissipation of Londax.

To test Londax persistence under California rice-field conditions, a commercial application of one ounce per acre was followed at a flooded field on the Rehmann Ranch near Biggs. Water was analyzed by HPLC (sensitivity 1 ppb); soil was extracted with ammonia, extracts concentrated, and aliquots analyzed by the HPLC method.

The dissipation curve for Londax in water (Fig. 6) shows that the initial high concentration (154 ppb) was reduced to half in 13 hours. However, as the dissipation did not follow first-order kinetics, a true "half-life" could not be determined. Within 6 days, the residue concentration fell to 22 ppb and was undetectable (<1 ppb) within 12 days. The concentration in sediment collected at the same locations as the water reached a maximum of 175 ppb at 67 hours (2.8 days) and then slowly declined to 85 ppb at 1416 hours (59 days).

The maximum theoretical homogeneous concentration in water would be 69 ppb, but the spray plane resprayed the borders of the test field at the place where sampling was in progress, accounting for the unusually high residues. Even so, at least half of the residue which reached the water remains unaccounted for.

3. Field Dissipation of Quinclorac.

Quinclorac was applied as 50% WP formulation at 0.9 lbs/acre a.i. to small test plots at the Biggs Research Station. The dissipation curve (Fig. 7) showed that concentrations in water declined rapidly from a maximum of 1190 ppb and 510 ppb in plots A and B, respectively, to less than 2 ppb (undetectable) in plot B over a period of 31 days.

The 75-85% decline of residues during the first day was not anticipated by the laboratory experiments. Quinclorac was not strongly bound to sediments, as confirmed by the low soil residues from field experiments (Fig. 8), and the herbicide appeared to be relatively stable in the submerged sediments. The initial loss may represent nothing more than dispersion from the concentrated solid formulation into the surrounding body of water, although high natural oxidant (such as H_2O_2) could account for part.

C. Objective III.

1. Persistence of thiobencarb in recirculating field water.

An attempt was made to compare the dissipation rate of thiobencarb (Bolero®) in recirculating water with that in an unrecirculated field. The experiment was conducted on the Mace Ranch (Natomas Central Mutual Water Co.) and an untreated field on Del Paso Road which is on the same water system. Duplicate samples were collected for analysis over a 98-day period as follows: Control soil from an adjacent field (A), control water from the system inlet (B), midsystem water (C), soil and water from the treated field (D,E), and water both as it entered the field (F), and left the field in a drainage ditch (G).

As shown in Table 3, thiobencarb residues in field water dissipated at the normal rate consistent with our previous observations on unrecirculated water.

TABLE 3. Thiobencarb Concentrations (ppb) within a Recirculating System

Elapsed Days ^a	Control Soil	Control Water	Midsystem Water	Field Soil	Field Water	Supply Water	Drainage Ditch
	A	B	C	D	E	F	G
9 ^b	<10	<5	<5	5310	151;148	<5	31
23	<10	<5	10	2020	18;15	<5	<5
37	<10	<5	<5	940	<5;<5	<5	<5
42	<10	<5	<5	1080	<5;<5	<5	<5
56	<10	<5	<5	550	<5;<5	<5	<5
70	<10	<5	<5	480	<5;<5	<5	<5
84	<10	<5	<5	530	<5;<5	<5	<5
98	<10	<5	<5	30	<5;<5	<5	<5

^aThiobencarb applied on 12 May 1987. ^bSpill began on 21 May 1987.

The soil again represented a thiobencarb reservoir; even after 3 months, soil residues of 30 ppb remained. However, recirculated water never contained detectable thiobencarb, and the drainage ditch water was thiobencarb-free within 2 weeks after field spillage began. Unfortunately, no corresponding unrecirculated field was sampled simultaneously, but results suggest that while recirculation appears to clean up field water effectively, it probably has no major effect on residue dissipation within the treated fields.

2. Destruction of rice herbicide spray waste.

According to CDFA, over 190,000 pounds of MCPA herbicide was applied to California rice in 1985, essentially all as dilute spray from aircraft. To determine if excess (waste) spray could be detoxified by sunlight in the presence of an hydroxyl generator, MCPA spray waste (obtained from Onstatt Air, Robbins, CA, or prepared as needed from commercial formulation) was treated with Clorox® hypochlorite bleach in polythene tubs either exposed to or protected from summer sunlight.

Dilute (100 ppm) solutions of MCPA dimethylamine salt broke down rapidly with bleach and sunlight but not with bleach in the dark. The MCPA spray waste (12,000 ppm) appeared to break down readily with bleach both with and without sunlight. Experiments are continuing.

3. Zinc oxide-catalyzed degradation of Basagran in rice fields.

Detection of bentazon residues in local water resulted in imposition of a highly restrictive holding period for treated field water. As bentazon was rapidly degraded by zinc oxide and UV radiation in the laboratory (Objective I), an attempt was made to determine the feasibility of degrading bentazon residues in the field by aerial application of the ZnO catalyst.

Water was drained from a series of test plots in a commercial rice field (Scheidel Ranch, Sutter Co.), Basagran was supplied as usual, the water was brought up over a period of 3 days, and ZnO was applied to two plots (B,C) by aircraft leaving two plots (A,D) as controls. ZnO appeared to immediately reduce by 20% the residues in water in treated plots (Fig. 8) but this effect was overcome within 2 days and bentazon levels then declined with a half-life on the order of 5 days. However, control plot A appeared to have received enough ZnO drift to behave like B and C, while control plot D suffered extensive bentazon loss perhaps due to some water management practice. Therefore, the results remain inconclusive.

PUBLICATIONS OR REPORTS

- D.G. Crosby and R.B. Draper. 1987. Catalyzed photooxidation of the herbicide molinate and thiobencarb. ACS Symposium Series, 327:240-247.
- D.G. Crosby and R.M. Higashi. 1987. A physical-chemical microcosm for ricefield environmental fate studies. In "Pesticide Science and Biotechnology" (R. Greenhalgh and T.R. Roberts, eds.), Blackwell Sci. Publ., 1987, p. 445-448.
- A.P. Toole and D.G. Crosby. Environmental fate studies of fenoxaprop-ethyl. Abstr. 193rd National Meeting, American Chemical Society, Denver, CO. April 1987.
- R.S. Tjeerdema and D.G. Crosby. 1987. The biotransformation of molinate (Ordram) in the striped bass (*morone saxatilis*). Aquatic Toxicology 9:305-317.

CONCISE GENERAL SUMMARY OF CURRENT YEAR'S RESULTS:

1. Thiobencarb (Bolero) residues in water and soil did not appear to dissipate significantly faster in a recirculating water system than in a field without recirculation, but recirculated water was residue-free. Reabsorption of thiobencarb and molinate from atmospheric vapor did not contribute measurable residues to clean water.
2. Ultraviolet radiation from sunlight was the principal cause of bentazon (Basagran®) field dissipation, whose normal half-life was 3-5 days. Three major bentazon transformation products were identified, two of which were degraded in sunlight and one of which was stable. Bentazon was rapidly photo-oxidized in the presence of zinc oxide in the laboratory, but attempts to use this technique to reduce field residues were inconclusive.

3. Londax was essentially stable to sunlight in aqueous solution; the manufacturer's claim of a 4-hour half-life was based on erroneous experiments. Although it dissipated from water with an initial half-life of 13 hours in a field trial, Londax was largely stable in the sediment, and the combined residues of soil and water accounted for less than half of the applied amount.
4. Both gas-and liquid chromatographic methods were developed for analysis of residues of quinclorac (BAS 514H) in soil and water down to the low ppb level. Although only slowly degraded by sunlight in the laboratory, initial loss of quinclorac residues in the field was rapid, probably due to redistribution into water. Quinclorac was not bound appreciably or degraded rapidly by sediment, and soil residues remained low. Dichloroquinoline was isolated as the only significant degradation product.
5. MCPA spray waste was effectively degraded by combined hypochlorite bleach and sunlight.

DGC:jg
comprehene.1

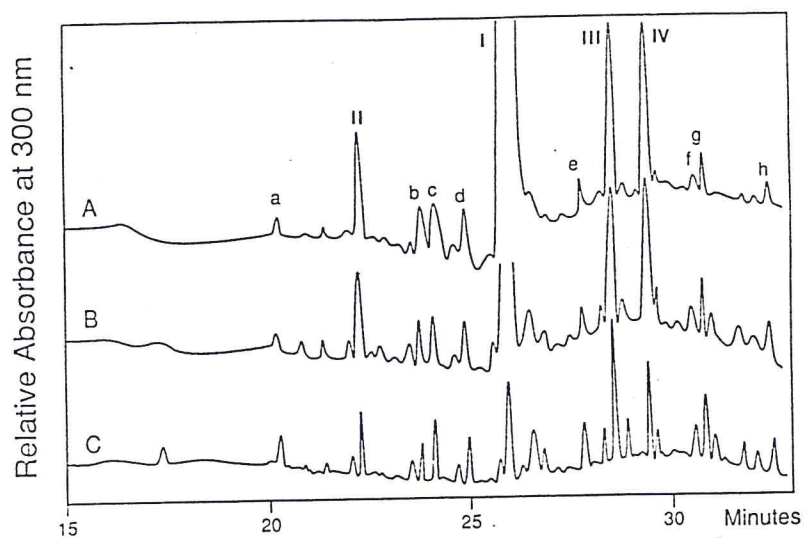


Fig. 1. Bentazon photoproduct mixture before purification (A), after crystallization of bentazon (B), and after HPLC (C).

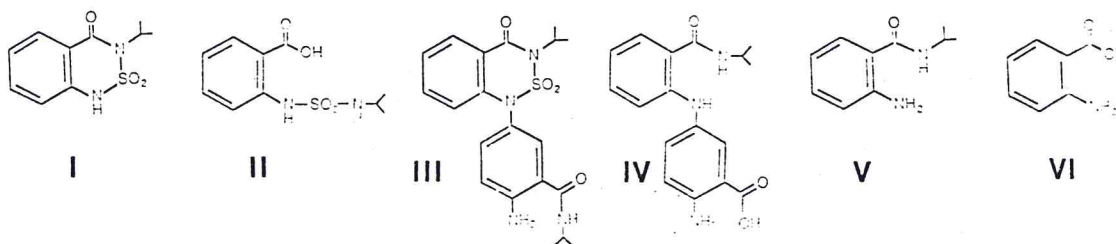


Fig. 2 Chemical structures of identified photoproducts.

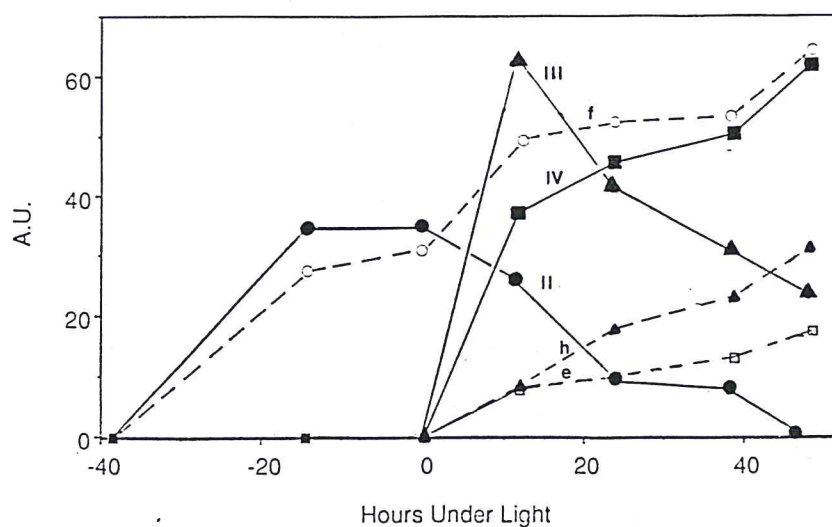


Fig. 3 Rates of formation and dissipation of photoproducts.

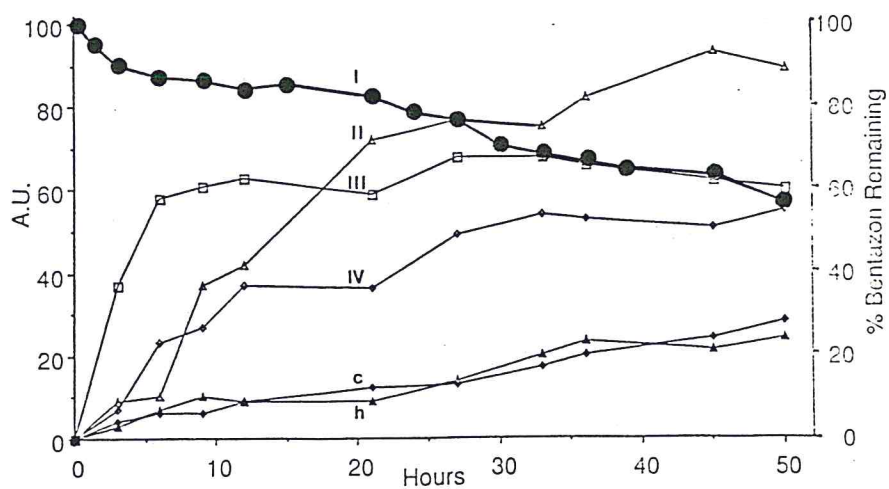


Fig. 4 Rates of formation of photoproducts in the field. Bentazon dissipation ●

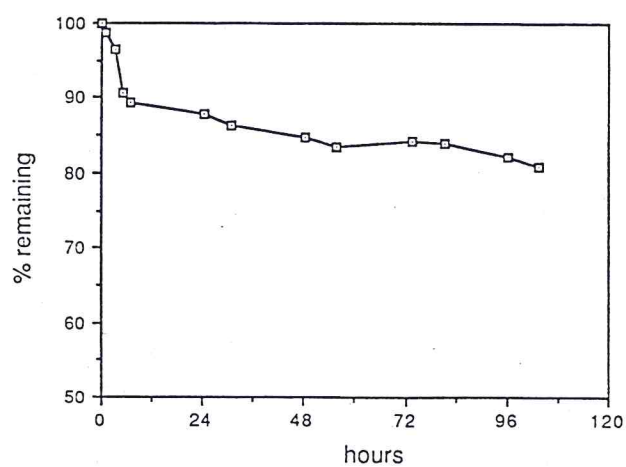


Fig. 5 Laboratory photodegradation of quinclorac.

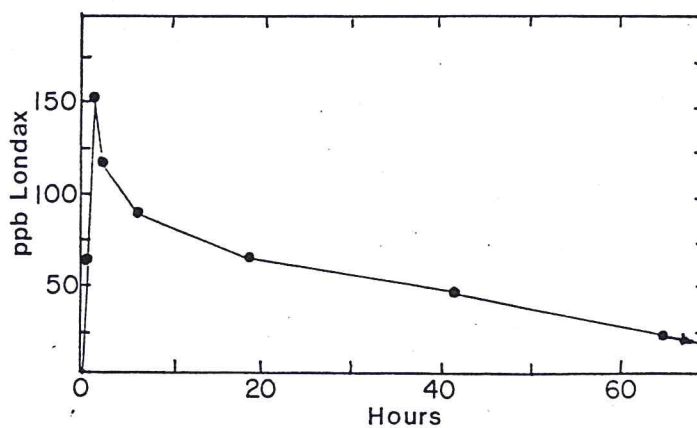


Fig. 6 Dissipation curve for Londax under field conditions.

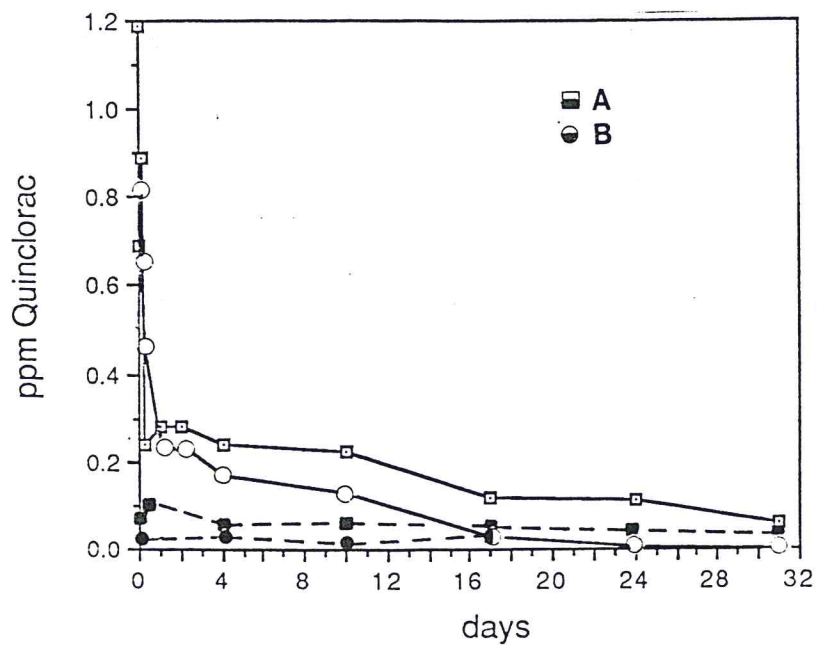


Fig. 7 Dissipation curve for quinclorac in water (open symbols) and soil (closed symbols) under field conditions in plots A and B.

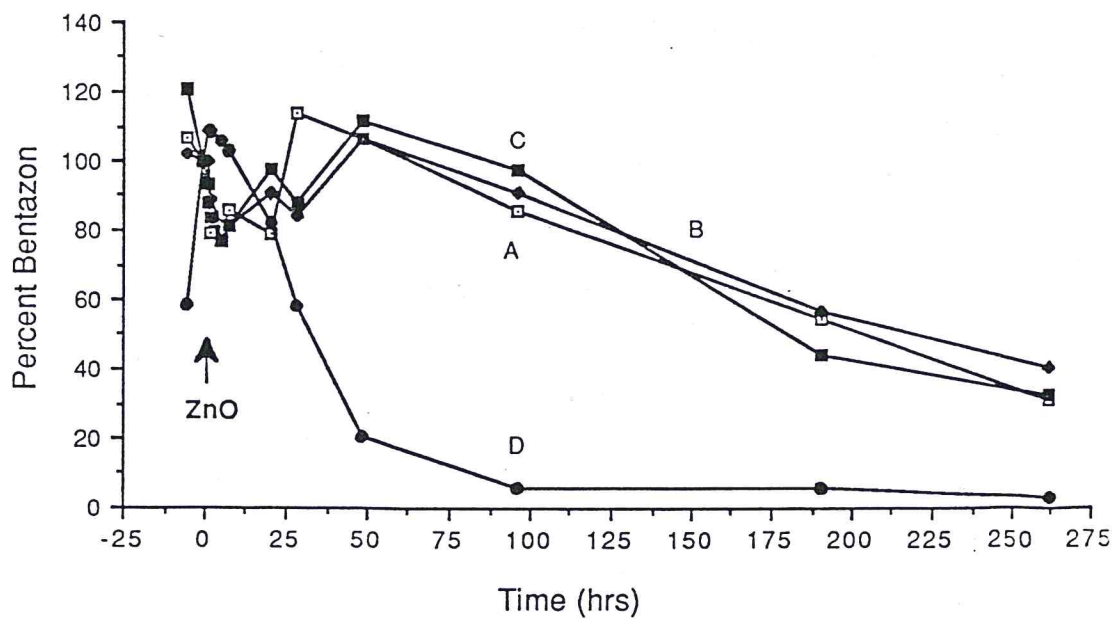


Fig. 8 ZnO-catalyzed photodegradation of bentazon in field plots B and C. Plots A and D were untreated controls.