

COMPREHENSIVE RESEARCH ON RICE
ANNUAL REPORT

January 1, 1985 - December 31, 1985

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

PROJECT LEADER AND PRINCIPLE UC INVESTIGATORS:

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LEVEL OF 1984 FUNDING: \$39,600

OBJECTIVES AND EXPERIMENTS CONDUCTED BY LOCATION TO ACCOMPLISHMENT OBJECTIVES:

- A. Objective I. To identify, investigate, and model environmental factors which govern movement and chemical fate of rice pesticides.
1. Catalyzed photo-oxidation of rice pesticides (UCD).
 2. Effect of pH on photo-oxidation rates (UCD).
 3. Photodegradation of fenoxaprop-ethyl (UCD; Rice Research Facility, Davis; Rice Research Station, Biggs).
 4. Photo-oxidation of Londax (UCD).
 5. Photodegradation of bentazon (UCD; Colusa Co.; Stanford University, Palo Alto).

- B. **Objective II.** To estimate the relative importance of such factors to the practical use of specific rice pesticides.
1. Field trial of ZnO-catalyzed degradation of thiobencarb (UCD; Rice Research Facility, Davis).
 2. Water management field trial (UCD; Colusa Co.).
 3. Microcosm experiments with soil (UCD).
 4. Molinate metabolism in fish (UCD).
- C. **Objective III.** To apply research results toward meeting regulatory requirements and improved management of rice pesticides.
1. Field trial on effects of ZnO on rice production (UCD; Rice Research Facility, Davis).

SUMMARY OF 1985 RESEARCH (MAJOR ACCOMPLISHMENTS) BY OBJECTIVE:

A. Objective I.

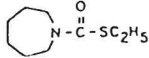
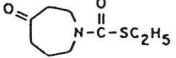
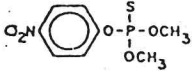

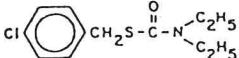
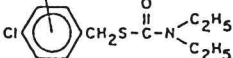
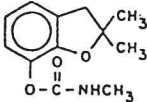
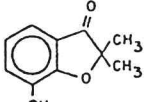
1. Catalyzed Photo-oxidation of Thiobencarb and Other Rice Pesticides.

In order to examine the semiconductor-catalyzed photo-oxidation of thiobencarb and other major rice pesticides more closely, aqueous solutions (4×10^{-5} M) were agitated with 100 mg/L of either titanium dioxide (TiO_2) or zinc oxide (ZnO), irradiated in a sunlight-simulating photoreactor for several hours while samples were collected and analyzed for parent pesticides, and the principal photodegradation products isolated and identified by mass spectrometry. Reaction rates were calculated and converted to half-lives.

The thiobencarb was of particular interest. Due to instability, its photo-oxidation products generally were converted to their dimethyl-tert-butylsilyl derivatives (1984 Report). *p*-Chlorobenzyl alcohol, *p*-chlorobenzaldehyde, *p*-chlorobenzoic acid, *p*-chlorobenzyl mercaptan, and a ring-hydroxylated thiobencarb were identified. *p*-Chlorobenzoic acid always constituted the largest proportion in the mixture of products. Thiobencarb sulfoxide and sulfone were too unstable to be isolated, but their presence could be inferred from the 1984 molinate experiments.

Table I shows the photo-oxidation half-life for each of the chemicals tested, together with the principle breakdown product (which themselves subsequently were degraded). The results indicate that all of the substances were subject to rapid, semiconductor-catalyzed photo-oxidation to products presently considered to be biologically inactive.

Table I. ZnO-catalyzed photooxidation of rice pesticides.

Pesticide	Half-life (minutes)	Major Product	Pesticide	Half-life (minutes)	Major Product
 Molinate	4	 4-keto molinate	 Methyl parathion	20	 4-nitro phenol
 Thiobencarb	11	 Hydroxy thiobencarb	 Carbofuran	16	 3-keto carbofuran phenol

2. Effect of pH on the ZnO-Catalyzed Photo-oxidation of Molinate.

While TiO_2 is known to be inert toward acid or base, ZnO dissolves in acid below pH 6 to form soluble zinc ion, in strong base to give a zinc hydroxide complex ion. Ultraviolet (UV) radiation increases the rate of dissolution. However, only solid ZnO can catalyze photo-oxidation. Consequently, the effect of pH on the rate of molinate photo-oxidation was measured in the manner shown in Section I but using buffers.

The results (Fig. 1) show that molinate is photo-oxidized very slowly below pH 7 (neutrality), but the rate increases steadily with increasing alkalinity. Measurements were not made above pH 10, as the pH of ricefield water seldom rises above this value. The data suggest that ZnO cannot be used as a photo-catalyst under acidic conditions, and oxidations will proceed only slowly at pH 7. As field water pH rises during the day due to algal photosynthesis, applications of ZnO should be timed to take advantage of both the sunlight intensity and high pH of midday.

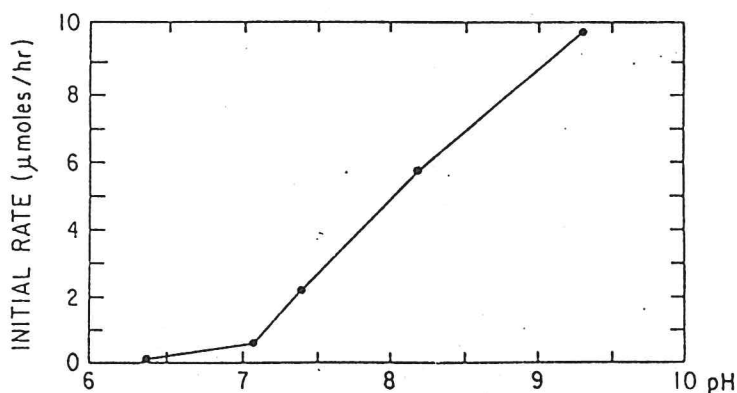


Fig. 1. Effect of pH on ZnO-catalyzed photo-oxidation of molinate.

3. Photodegradation of Fenoxaprop-ethyl (Whip^R).

Fenoxaprop-ethyl (HOE 33171), a phenoxyester herbicide formulated as Whip^R, has shown promising results for selective control of weed grasses in flooded rice. In order to investigate the environmental persistence of phenoxaprop-ethyl under California conditions, both the technical grade and the usual formulation were tested under both laboratory and field conditions.

Initially, it proved necessary to develop analytical methods for the herbicide and its expected degradation products in water and soil at part-per-billion levels; this was accomplished with both gas chromatography (GLC) and high-pressure liquid chromatography (HPLC). Based on this, the UV photolysis half-lives for solutions of fenoxaprop-ethyl in distilled and field water in the photoreactor were determined to be 43.6 and 13.8 hrs, respectively. The presence of a 750-fold molar excess of the ricefield photo-oxidant hydrogen peroxide or its ester, potassium persulfate, in distilled water solutions of the herbicide reduced the half-life to less than one hour. With as little as a 15-fold molar excess of potassium persulfate, the half-life was still less than two hours.

Hydrolysis, as well as photolysis, was found to be a significant factor affecting the fate of fenoxaprop-ethyl, especially at basic pH. Aqueous solutions of the chemical, buffered to pH 6.1 or 7.4 and kept in the dark showed little breakdown after 68 hours (Fig. 2); at pH 9.1, the half-life fell to 8.3 hrs. The major hydrolysis products identified by thin layer chromatography and mass spectrometry were 6-chlorobenzoxazol-2-one and the free acid corresponding to fenoxaprop-ethyl. Neither product accumulated in irradiated solutions, apparently being more quickly photolyzed than the parent to simpler products.

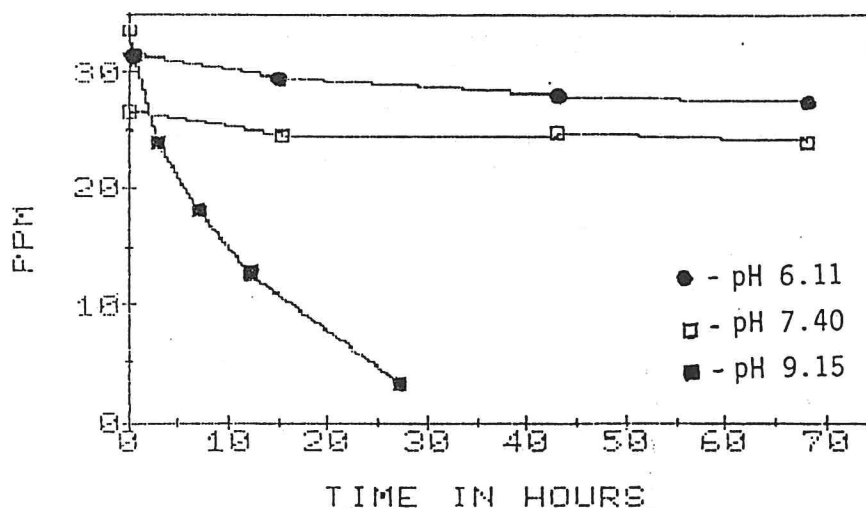


Fig. 2. Hydrolysis rates of fenoxaprop-ethyl in buffer at three pH values.

The Henry's Law constant for fenoxaprop-ethyl, which predicts its tendency to evaporate from water, was calculated from physical constants provided by the manufacturer (American Hoechst) to be 7.7×10^{-7} atm-m³/gm-mole; it should be essentially nonvolatile. The scenario which emerges suggests that breakdown of the herbicide in a sunlit field where pH becomes alkaline at midday should be rapid.

Two sets of field studies were carried out. The first was at the Biggs Rice Research Station, where Whip was applied to 3" of water (pH 6.6 - 8.3) in 13' x 18' rice plots separated from each other by small dikes. Regular water sampling of one plot followed by analysis showed a half-life for fenoxaprop ethyl of 2.2 hrs (Fig. 3). While some dissipation was attributable to dilution from adjacent plots, a study in aluminum rings at the Davis Rice Research Facility supported the finding that the disappearance indeed was rapid. Whip was applied to water 8 cm deep (pH 8.9 - 9.3) contained within 4.5 m² rings set in a flooded rice field; the half-life in the water in this case was 2.6 hrs (Fig. 4). Again, neither the fenoxapropacid nor 6-chlorobenzoxazole-2-one were detected in any of the field water samples. Wet soil samples from the Davis experiment had relatively high concentrations of fenoxaprop-ethyl --269 ppb at 6 hrs and 339 ppb at 30 hours after application -- indicating that soil adsorption is a major process affecting the fate of the chemical. However, only 18 ppb could be recovered from the soil after 144 hours (6 days), and none could be detected in subsequent samples. Studies of the compound's fate in soil are continuing.

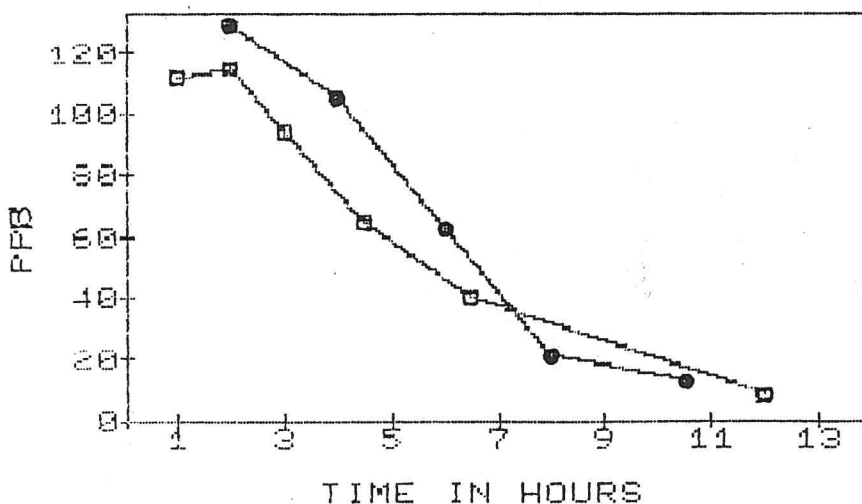


Fig. 3. Photodegradation of fenoxaprop-ethyl (Whip) in field plots at Biggs (●) and the UCD Rice Research Facility (□). Biggs values are x 3.

4. Photodegradation of Londax.

Londax is an experimental herbicide from DuPont which shows promise for control of broad-leaf weeds in California rice. As presented briefly in our 1984 Rport, Londax showed low volatility and did not degrade during 4 days in distilled water under UV irradiation in the photoreactor, suggesting possible environmental persistence.

Experiments with Londax proved difficult because of its low solubility in water (80 mg/L at pH 7) and the low application rates expected in the field. Londax was not volatile enough to permit GLC analysis, but HPLC provided satisfactory results at 1-10 $\mu\text{g/L}$ (ppb) by using a prior isolation from water onto a C-8 Bond-Elut resin cartridge. Although stable to UV irradiation in distilled water, Londax underwent UV degradation in the presence of 500 mg/L (15 μM) aqueous hydrogen peroxide (Fig. 4); at 50 mg/L of peroxide--still a very high environmental level--degradation was much slower.

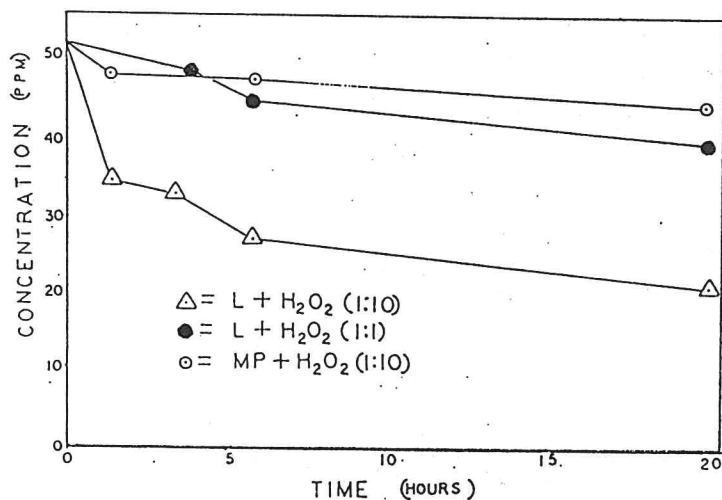


Fig. 4. Photodegradation of Londax in aqueous hydrogen peroxide. MP = monomethyl phthalate.

However, when irradiated in water (pH 7.5) from the UCD Rice Research Facility, about 33% of the Londax could be seen eventually to dissipate within 45 days, and the rate of loss became substantially greater in phosphate buffer (pH 7.5), 33% dissipating within about 20 days (Fig. 5). This means that Londax still would be essentially stable toward the usual forces of light, pH, and volatility during its practical residence in the rice field environment.

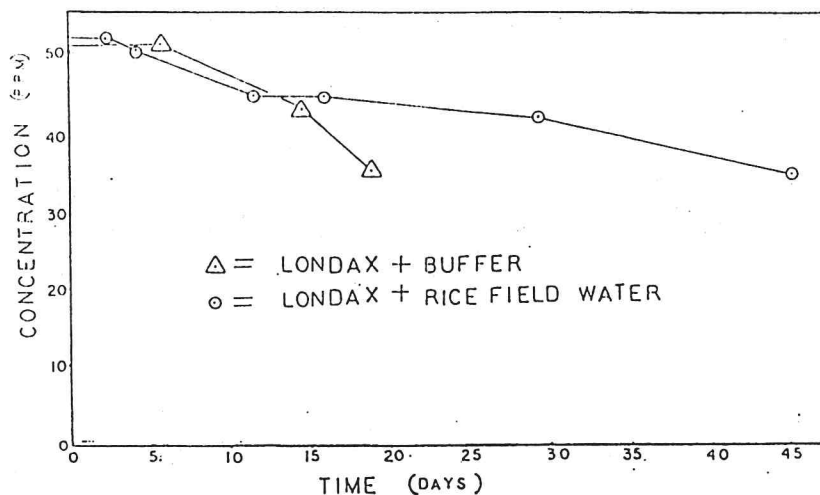


Fig. 5. Photodegradation of Londax in buffer and field water in the photoreactor (pH 7.5).

In order to seek Londax photodegradation products, the technical herbicide was irradiated in $15 \mu\text{M H}_2\text{O}_2$ for about 6 hrs until 50% of the starting material was gone. In addition to artifacts seen in the controls, several HPLC peaks represented breakdown products; no GLC responses were observed, so these products presumably were not volatile. A ureasulfonic acid was separated by GLC from the methylated reaction mixture, but the expected companion--monomethyl phthalate--was not observed under any experimental conditions, although a synthesized standard proved to be quite stable under irradiation (Fig. 4).

When Londax was irradiated in bicarbonate buffer until 90% was degraded, gravimetric analysis showed that about 50% of the sulfur atoms were present in solution as sulfate, indicating extensive Londax breakdown, but still no phthalic acid or esters could be detected.

5. Photodegradation of Bentazon.

Bentazon (Basagran) is a major rice herbicide in California. Its photodegradation was reported in 1975 by scientists at Michigan State University but under environmentally unrealistic conditions. To examine bentazon degradation in relation to rice field conditions and apply the results to microcosm development, both laboratory and field studies were commenced. Bentazon was photodegraded with a half-life of 3.3 days in rice field water and 4.1 days in distilled water in the laboratory. Products were isolated by extraction onto C-8 resin cartridges, derivatized with MTBSTFA (1984 Report), and analyzed by capillary GLC; 7 complex products were detected whose proportions varied with irradiation period.

Replacement of cartridge extraction with lyophilization before derivatization revealed at least 26 products, while use of HPLC instead of GLC allowed separation of 24 products. These were collected laboriously from the HPLC effluent, and presently are undergoing structural analysis by high-resolution NMR spectrometry (using an instrument at Stanford University) and mass spectrometry.

The field dissipation of bentazon was measured in a 10 x 20 ft plot in a larger field treated with Basagran. The results (Fig. 6) indicate a half-life in water of 2.9 days and a steady concentration in soil over the 50 hours following Basagran application. Scale expansion showed that most of the dissipation occurred during daylight (half-life 1.5 hours), consistent with laboratory photodegradation results.

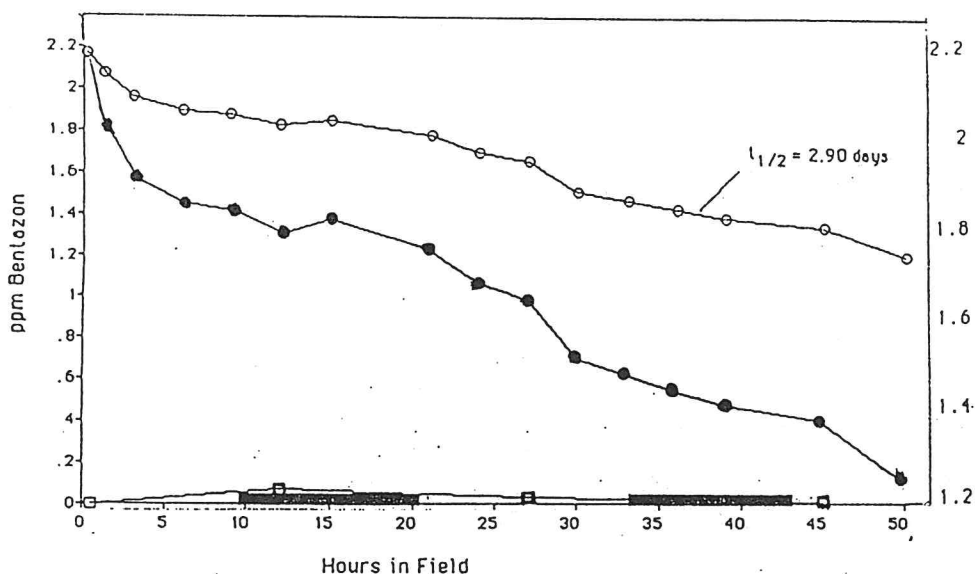


Fig. 6. Field dissipation of bentazon in water on a normal (O) and expanded (●) scale, and in soil (□). Night = ■

B. Objective II.

1. Field Trial of ZnO-Catalyzed Photo-oxidation of Thiobencarb.

To verify the laboratory observations on the enhanced photo-oxidation of thiobencarb, small-scale plots (4.5 m²) in a larger rice field were confined by aluminum rings to provide water about 10 cm (4 in) deep. The plots were treated with thiobencarb at 5.6 lbs/acre (6.3 kg/ha) as Bolero 10 G; pH, temperature, dissolved oxygen, thiobencarb, thiobencarb sulfoxide, p-chlorobenzaldehyde, and p-chlorobenzoic acid, and dissolved zinc were monitored in the water. After 74 hrs (3 days), a 1 g/L water-suspension of ZnO corresponding to 3, 6, and 12 kg Zn/ha (2.7, 5.3, and 10.7 lbs/acre) was applied, and water monitoring was continued.

The dramatic effect of ZnO of thiobencarb levels in comparison with untreated controls is shown in Fig. 7 (next page). At 12 kg Zn/ha, thiobencarb residues decreased 93% within 2 hours, with proportionate decreases at the lower ZnO application rates. However, it is apparent from the controls that even after 3 days, herbicide levels still were increasing as thiobencarb continued to be released from the Bolero granules or soil. This is an obvious and correctable source of thiobencarb persistence. The worrisome thiobencarb sulfoxide formed before ZnO application dissipated quickly (Fig. 8) but slowly increased again as fresh thiobencarb came off the granules; sulfoxide continued to rise to a maximum of 64 ppb in controls. p-Chlorobenzaldehyde levels remained low, and the nontoxic p-chlorobenzoic acid steadily declined.

Zinc levels also declined continuously, and from the beginning lay far below the theoretical maximum values (Table II). Even in the field water, Zn was far below the U.S. Water Quality Criteria value for drinking water (5.0 ppm) and probably was below the value for the exposed fish species (1% of the 96-hour median toxic concentration). However, the zinc concentration in drainage and river water cannot presently be predicted, and salmonid fish are unusually sensitive to it.

Table II. Zinc levels in water from thiobencarb residue photo-oxidation.

Treatment (kg Zn/ha)	Theoretical Maximum (ppm)	Zn Residue, ppm (mg/L)			
		0	0.2	2	5 days
0	0.0	<0.01	<0.01	<0.01	<0.01
3	3.0	<0.01	0.20	0.07	0.02
6	6.0	<0.01	0.30	0.10	0.03
12	12.0	<0.01	0.43	0.42	0.14

2. Sampling and Analysis of Molinate Field Residues.

In a follow-up of the 1984 Colusa Water Management trials described briefly in last year's report, the effect of water depth and holding period on molinate residues in water was reexamined and extended. All together, over 300 samples were analyzed by the improved GLC procedure described last year, representing 28 test plots and 4 water inlets. Our results, to be reported in detail to the Water Resources Control Board, are summarized in Appendix I.

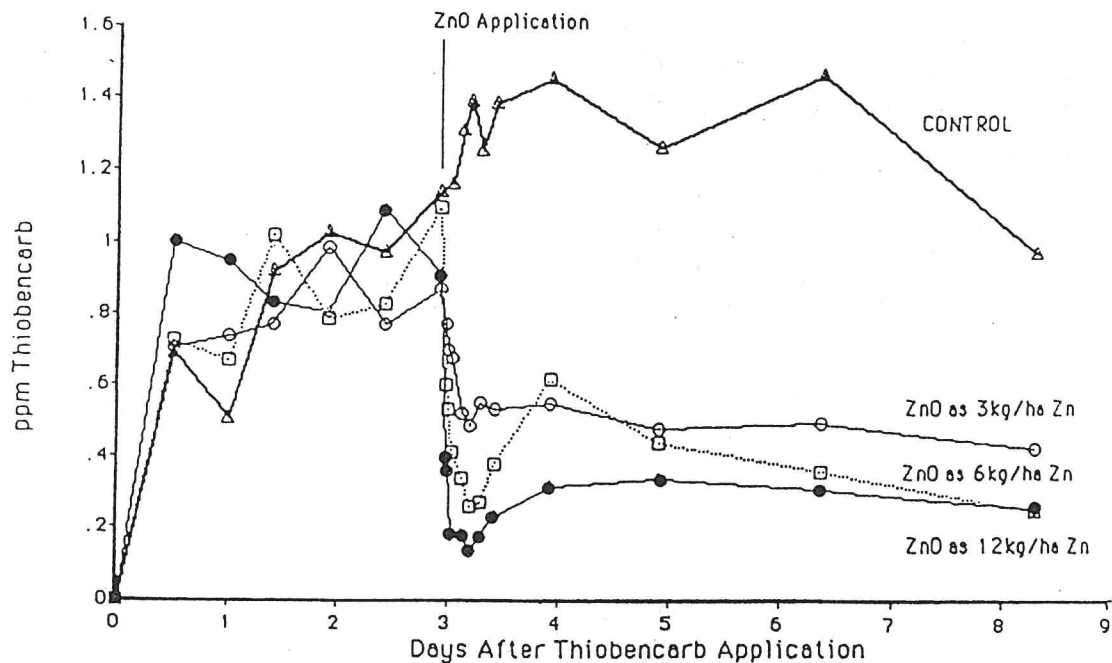


Fig. 7. Effect of ZnO on thiobencarb dissipation rate.

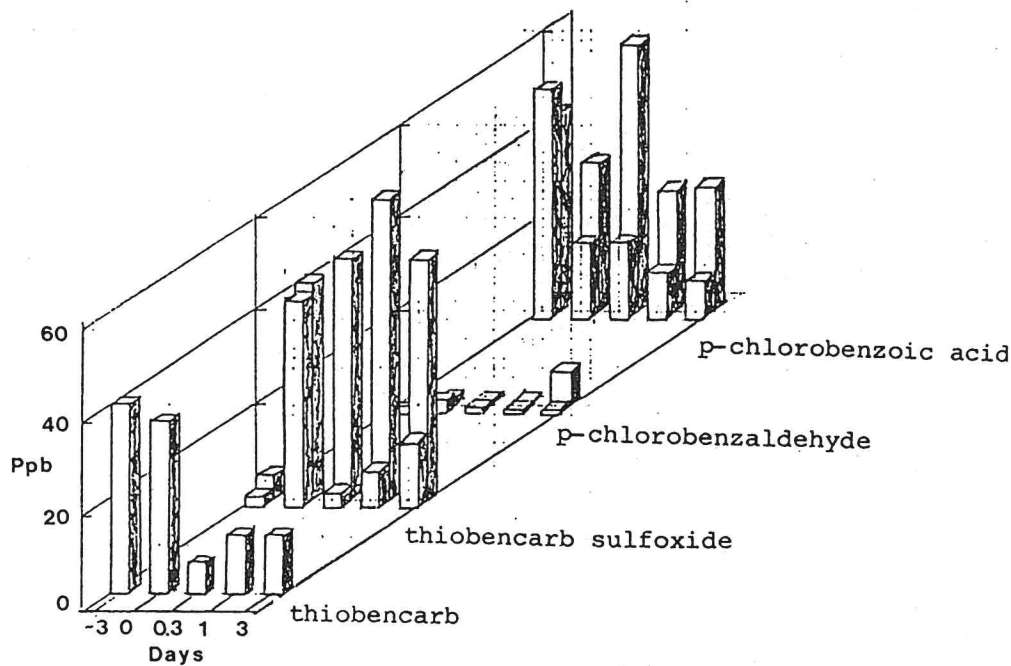


Fig. 8. Residues dynamics of thiobencarb and its photodegradation products. Front bar represents 12 kg/ha Zn, rear bar represents no-Zn control.

The principal conclusions are (1) that water-holding depth determines initial molinate residues -- the deeper the water, the lower the residue -- but that within an 8-day holding period residues become independent of depth (Fig. 9); (2) water management following the holding period has little influence on either molinate dissipation rate or discharge level; (3) dissipation rates (half-lives), alone, may not accurately predict what the residue level will be at the time of water release; (4) short-term fluctuations in residues drastically affect both the precision and accuracy of analytical results, meaning that random water-sampling can lead to very erroneous estimation of average molinate levels; and (5) preflood application of Ordram results in molinate residues generally less than 2% of those from post-flood application, suggesting further consideration of this practice.

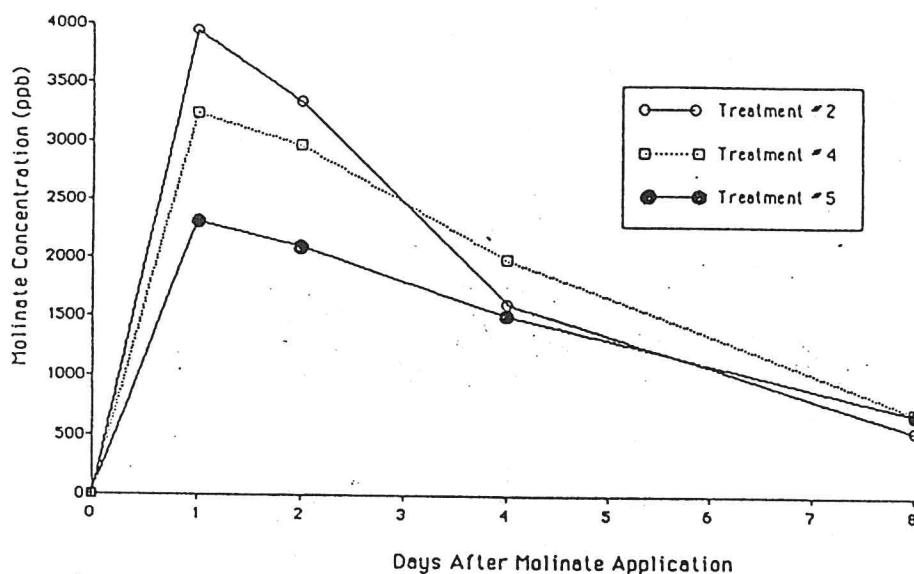


Fig. 9. Molinate dissipation rates at average water depths of 3 (○), 4.5 (□), and 6 (●) inches.

One plot planned for pre-flood treatment did not receive any Ordram but still showed substantial residues (115 ppb) after flooding. By high-resolution capillary GLC, two-thirds of the response could be ascribed to an interfering substance -- picked up by the field water at flooding -- which possessed the same analytical properties as molinate. Identification of the unknown substances is in progress, and as it was present in all of the pre-flood application samples, further investigation of its source and occurrence are deemed important.

3. Microcosm Experiments with Soil.

For measurement of a mass balance of molinate between water and air in the laboratory rice-field microcosm, water samples were removed at intervals and extracted through Bond-Elut C₁₈ cartridges, while air samples were collected in the outlet system via amberlite XAD-4 resin. GLC analysis showed that >99% of the molinate could be accounted for.

Rice field soil was collected, air-dried, ground, mixed, sieved, and stored in covered containers. A sample of the soil was placed in the microcosm to a depth of 1 inch, water added, and the mass balance experiment repeated. Addition of soil did not perturb the molinate concentration profile but reduced the maximum water residue by about 10%, consistent with theory. This prepares the microcosm for later field-simulation experiments.

4. Molinate Metabolism in Fish.

One of the principal reasons behind the public furor over rice herbicides has been the reported kills of common carp (Cyprinus carpio) in agricultural drains during the peak period of molinate application. Curiously, other fish species also reside in the drains but seldom seem to be affected. To investigate this peculiarity, a fish metabolism chamber was designed and constructed which would permit exposure of animals to radiolabelled molinate and quantitative recovery of metabolites and unmetabolized herbicide. A method was devised to separate and identify metabolites by HPLC, and metabolite standards were synthesized or obtained from the Stauffer Chemical Company.

The initial comparison has been between carp and striped bass (Morone saxatilis), and the results are shown in Table IV. The principal metabolic difference between the two species appears to be the excretion of molinate sulfoxide by the bass -- perhaps enough to account for the notable difference in molinate toxicity but probably not. Another resistant species, white sturgeon (Acipenser transmontanus), presently is undergoing the tests, and work on the biochemical mechanism of molinate toxicity will start soon. This work, by Rön Tjeerdema, is primarily supported by NIH and SWRCB.

TABLE I. Comparison of the metabolite profiles for striped bass and carp.

Compound	Depurated ¹⁴ C			
	Striped bass		Common carp	
	nmol/g	%	nmol/g	%
Molinate mercapturate	0.01 (0.01)	0.07	0.55 (0.25)	3.68
Polar conjugate	-- --	--	0.08 (0.03)	0.53
* Molinate sulfoxide	2.07 (1.53)	13.87	0.08 (0.02)	0.53
Hexamethyleneimine	0.01 (0.01)	0.07	0.23 (0.08)	1.54
4-Ketomolinate	0.02 (0.01)	0.13	0.30 (0.04)	2.01
4-Hydroxymolinate	0.11 (0.05)	0.74	0.83 (0.07)	5.55
Carboxymolinate	0.61 (0.18)	4.09	0.46 (0.06)	3.08
Molinate	12.09 (1.70)	81.03	12.42 (2.74)	83.08

Objective III.

1. Effects of ZnO on Rice Production.

A small-plot field test was conducted at the UCD Rice Research Facility to determine if a late application of ZnO could substitute for the usual zinc sulfate pre-flood treatment, avoid harmful effects on rice yield and quality, and still permit adequate weed control. A total of 32 field basins, 10 x 20 ft, were prepared and divided into 8 blocks of 4; half the blocks were treated with zinc sulfate (3 lbs Zn/acre), and the field was flooded and planted with M-101 short-statured rice at 200 lbs/acre.

At the rice 3-leaf stage, weeds were surveyed and molinate was applied at 5 lbs/acre (104 g/basin) as Ordram 10G; pH, temperature, and dissolved oxygen were monitored intensively; and water was sampled at regular intervals and analyzed for molinate. After 74 hrs (3 days), zinc was applied as zinc oxide or zinc sulfate at 6 lbs Zn/acre (6.72 kg Zn/ha) on Zn-pretreated basins and 9 lbs Zn/ha (10.08 kg Zn/ha) on basins not pretreated, and water was monitored intensively. At the end of the season, weed control and rice growth and yield were evaluated.

pH varied between 7.3 and 8.5, depending on time of day, water temperature ranged from 15 to 30°C (abnormally cold), and dissolved O₂ (7-18 ppm) was normal. However, loss of molinate was exceptionally rapid (Fig. 10A), apparently due largely to seepage through the sandy soil. Although the molinate residues at the time of ZnO application (74 hours) were low, the expected rapid photo-oxidation still could be discerned (Fig. 10B), the half-life being reduced from 22 hours to 2.1 hours.

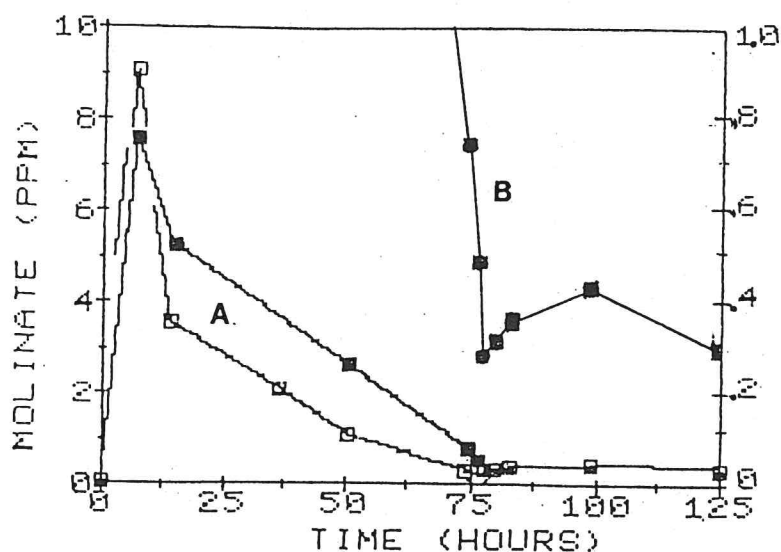


Fig. 10. Molinate dissipation rates, control (□) and ZnO-treated at 6 lbs Zn/acre (■), normal (A) and expanded (B) scales.

The October 31 harvest results are summarized in Table V. Pretreatment of plots with Zn resulted in significantly shorter plants except when additional ZnSO₄ was supplied later. However, there was no significant difference in rice yield between any of the treatments, although yields from plots not receiving weed control tended to be smaller than the others. Lodging, evaluated on an arbitrary scale from 1 (no lodging) to 99 (100% lodged) did not vary in any systematic way and was uniformly very slight only 2 weeks before harvest. Barnyard-grass control was virtually complete under all treatments, largely reflecting the very sparse weed stand at the beginning of the trial. Zinc levels in the water remained at <0.01 ppb in a control plot, reached 4000-6000 ppb immediately after Zn application, and then rapidly subsided (to 300-500 ppb within 1 day).

Although this trial was far from ideal, it indicated that neither ZnO nor the resulting photo-oxidant was harmful to the rice crop under these conditions and that ZnO probably can replace ZnSO₄ as a nutritional supplement.

Table V. Effect of zinc oxide treatment on rice production.

No.	Pre-Zn ^a	Treatment ^b	Height (cm)	Rice Yield ^c (lbs/acre)	Moisture ^c (%)	Lodging (1-99)	% BYG Control ^d
1	No	No M	72.8±3.2	5970±280	15.8±0.3	68	100
2	No	M Only	75.0±2.5	6780±110	15.4±0.2	54	93
3	No	M, ZnO	76.5±2.3	6520±150	15.5±0.1	60	98
4	No	M, ZnSO ₄	70.5±4.2	6760±240	15.2±0.4	41	99
5	Yes	No M	68.5±2.3	5190±590	16.2±0.4	32	91
6	Yes	M Only	67.5±2.7	6170±460	16.2±0.7	34	96
7	Yes	M, ZnO	70.0±1.6	5470±980	16.0±0.4	27	97
8	Yes	M, ZnSO ₄	70.5±4.3	5910±830	16.0±0.2	45	96

^a Preflood incorporation of Zn. ^b M = molinate as Ordram 10G.

^c Corrected. ^d Barnyard grass reduction.

PUBLICATIONS OR REPORTS:

1. R.B. Draper and D.G. Crosby. 1985. Enhanced photo-oxidation of rice herbicides. Abstr. 189th National Meeting, American Chemical Society, Miami, FL, April, 1984.

CONCISE GENERAL SUMMARY OF CURRENT YEAR'S RESULTS:

The photo-oxidation of molinate in sunlight, catalyzed by titanium dioxide (TiO_2) or zinc oxide (ZnO), has been extended to thiobencarb and other rice pesticides; in each case, the half-life was reduced to a few minutes, indicating broad applicability for this method of residue destruction. While TiO_2 was stable, the action of ZnO depended upon pH; it did not function below pH 7 (acidic), but its catalytic effect improved with increasing (alkaline) pH up to the field maximum at about pH 10. Rice field water becomes more alkaline toward midday, the optimum time for ZnO application. A limited field trial was conducted with thiobencarb, with ZnO applied at 3, 6, and 12 kg Zn/ha. The thiobencarb residue immediately dropped 93% at the highest Zn level and correspondingly in the others; however, it soon increased again as the Bolero granules and soil continued to release herbicide. In fact, the release in controls still was not complete at the end of the experiment (9 days), one obvious reason for thiobencarb persistence problems.

The 1984 water management field trial with Ordram in Colusa County was extended. Molinate residues initially varied inversely with water depth, but within an 8-day holding period they became independent of depth. Water management after the holding period had no influence on residues. It again was apparent that the exact time of day at which water samples are removed for analysis greatly affects the residue results. Preflood application of herbicide warrants more attention, but residue values may be high due to an interfering substance which mimics molinate. ZnO applied at 6 lbs Zn/acre to Ordram-treated rice plots reduced the half-life by 90%, and the ZnO treatment did not harm the rice yield or adversely influence weed control.

In environmental degradation experiments, Londax appeared quite persistent (half-life in field water >45 days in sunlight); irradiation in the presence of oxidant (hydrogen peroxide) produced similar results, and several degradation products were detected. At the other extreme, fenoxaprop-ethyl (Whip) decomposed rapidly in both the photoreactor and field plots (half-life 2.6 hrs) due to photolysis and chemical hydrolysis. Bentazon (Basagran) showed intermediate persistence (half-life of 2.9 days in field plots) and over 20 complex breakdown products.

APPENDIX I.

SUMMARY OF MOLINATE RESIDUES IN POSTFLOOD-APPLIED PLOTS

TREAT- MENT ^a	DEPTH (Inches)	WHP ^a DAYS	AVERAGE MOLINATE CONCENTRATION (ppb) PER 3 PLOTS ON DAY [#]									t _{1/2} ^b (days)
			Bkod	1	2	4	8	12	16	24	32	
1	5-7	8		1880 ^c ±115	1810 ±88	1290 ±94	543 ±82	185 ±29	52 ±10	21 ±5	5 ±2	3.48 ±0.19
2	1-3	8	2	3950 ±561	3340 ±272	1610 ±131	553 ±128	148 ±12	78 ±9	27 ±4	8 ±5	3.80 ±0.48
3	5-7	8		2230 ±460	2150 ±317	1720 ±150	533 ±34	204 ±58	57 ±30	25 ±7	8 ±4	3.59 ±0.28
4	3-5	8		3250 ±145	2970 ±143	2000 ±56	713 ±114	357 ±39	85 ±19	32 ±2	10 ±2	3.54 ±0.12
5	5-7	8	7	2310 ±98	2100 ±112	1520 ±95	703 ±95	339 ±52	88 ±14	26 ±2	6 ±1	3.50 ±0.06
6	5-7	16	2	2180 ±127	2120 ±243	1470 ±119	603 ±126	325 ±87	152 ±48	38 ±11	8 ±1	3.79 ±0.20
7	5-7	32		2250 ±106	2300 ±235	1630 ±78	643 ±145	367 ±87	173 ±36	53 ±4	12 ±3	4.07 ±0.20
8	5-7	8	8	2410 ±151	2320 ±155	1660 ±111	677 ±99	nd ^d	nd ^d	31 ±5	11 ±3	3.81 ±0.21

^a Water holding period.

^b t_{1/2} was determined by averaging rates from the least-squares fit of each plot's data from day 1 to day 32.

^c Boldface = residues during water holding period, ± standard error.

^d nd = not determined, due to dry field.