

COMPREHENSIVE RESEARCH ON RICE
ANNUAL REPORT

January 1, 1986 - December 31, 1986

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

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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. Effect of light intensity on photocatalysis (UCD).
 2. pH survey of rice-growing locations (Sacramento Co.; Sutter Co.; Butte Co.; Colusa, Co.).
 3. Persistence of Londax (UCD; Rice Research Station, Biggs; CSU-Chico).
 4. Persistence of bentazon (UCD; Stanford University, Palo Alto).

- B. Objective II.** To estimate the relative importance of such factors to the practical use of specific rice pesticides.
1. Mass-balance field trial of ZnO-catalyzed degradation of thiobencarb (UCD; Scheidel Ranch, Sutter Co.).
 2. Toxicity of zinc to ricefield organisms (UCD; Scheidel Ranch, Sutter Co.).
 3. Environmental persistence and degradation of fenoxaprop-ethyl (Whip) (UCD: Scheidel Ranch, Sutter Co.).
 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 trials on effects of ZnO on thiobencarb residues in water (UCD; Dennis Ranch, Colusa Co.; LeGrand Ranch, Colusa Co.; Tennis Ranch, Butte Co.; Boerger Ranch, Butte Co.; Dubois Ranch, Sacramento Co.).

SUMMARY OF 1986 RESEARCH (MAJOR ACCOMPLISHMENTS) BY OBJECTIVE:

A. Objective I.

1. Effect of light intensity on photocatalysis. Light absorption by photocatalysts such as ZnO and TiO₂, and the influence of light intensity upon it, are important to environmental applications; cloudiness is a normal occurrence in the Central Valley during May and June which could interfere with photocatalysis. A literature search showed that both catalysts absorb light near 370 nm, well into the sunlight region of the spectrum. The influence of ultraviolet (UV) intensity on the half-life ($t_{1/2}$) of 12 ppm aqueous thiobencarb in the presence of ZnO was determined both in the laboratory and under outdoor conditions. As briefly summarized in Table 1, some cloudiness could be tolerated, but the time required for photo-oxidation was lengthened considerably.

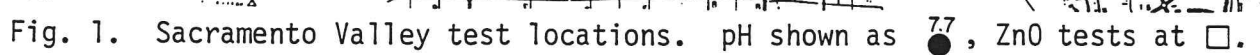
Table 1. Effect of light intensity on ZnO photocatalysis.

UV Intensity $\mu\text{W}/\text{cm}^2$	% of Full Intensity	Thiobencarb $t_{1/2}$ (min)	Outdoor Conditions
4000	100	142	Full sun (April
2200	55	202	Haze
1500	38	325	High clouds
500	13	>800	Overcast
200	5	>800	Heavy clouds, rain

2. pH Survey of rice-growing locations. In our 1985 Report, we showed that ZnO photocatalysis does not work at pH 7.0 or below. A survey of rice-field water, mostly between 10 a.m. and 3 p.m. on 12 June 1986, showed that almost all locations tested were above pH 7 except for several on the east side of the Sacramento Valley (Fig. 1, p. 4). However, individual fields still should be tested (with pH indicator strips) if the use of ZnO were contemplated.
3. Persistence of Londax. Field persistence of Londax herbicide was determined in experimental plots at the Biggs Rice Research Station. Londax was applied at 1 oz/acre to the flooded field, one-liter water samples were collected over an 8-day period, passed through a C₈ Bond-Elut resin cartridge to extract the herbicide, eluted with one mL of methanol, and analyzed by HPLC (C₁₈ reversed phase; aqueous methanol); limit of detectability was 3 ppb. If all of the applied Londax were dissolved in water 4" deep, the concentration would be 70 ppb; however, the herbicide was almost undetectable (5-8 ppb) within 8 hours and became undetectable within 8 days. Standard solutions containing 10 ppb of Londax in 0.01 M sodium bicarbonate (pH 8) were easily measured. Similar experiments (3 plots) with Londax-treated rice seeds showed no detectable herbicide in the water over a 30-day period except for one spurious peak, near the limit of detection, on Day 11 after planting.

Soil samples from the Londax-treated fields were cultured in both nutrient-rich and nutrient poor sterile liquid media containing Londax at 18°C and 37°C; although four different (unidentified) species of bacteria were isolated, HPLC analysis showed no evidence of microbial degradation of the herbicide. Repetition of the laboratory photolysis experiments reported last year showed eventual photodegradation at pH 8 in both phosphate and bicarbonate buffer (Fig. 2). The bicarbonate solution, analyzed by barium sulfate turbidity after 64 days in sunlight and 50% Londax degradation, showed 10% of the original sulfur to be in the form of sulfate. HPLC analysis revealed at least 8 different products in the pH 8 solution, the major one of which was isolated; the acidified solution provided another. Neither has yet been identified. As Londax is not degraded readily by either microorganisms or sunlight and yet virtually disappears from field water within 8 hours, rapid uptake by plants and/or soil must take place. Despite the apparent persistence, the rapid loss of Londax from water is attractive.

4. Persistence of Bentazon (Basagran). In 1985, we reported the half-life for bentazon in a rice field as 2.9 days. That dissipation rate has been successfully modelled in the laboratory microcosm using temperature programming and UV light (F40BL lamps) set to simulate field conditions (Fig. 3). As with molinate, it was found that operating the microcosm at a constant (average) rice-field temperature of 23.5°C produced a half-life significantly longer than observed in the field (Table 2). The microcosm has been improved by addition of the UV lamps, computer monitoring of air temperature, relative humidity, and pH, and numerous changes in software.



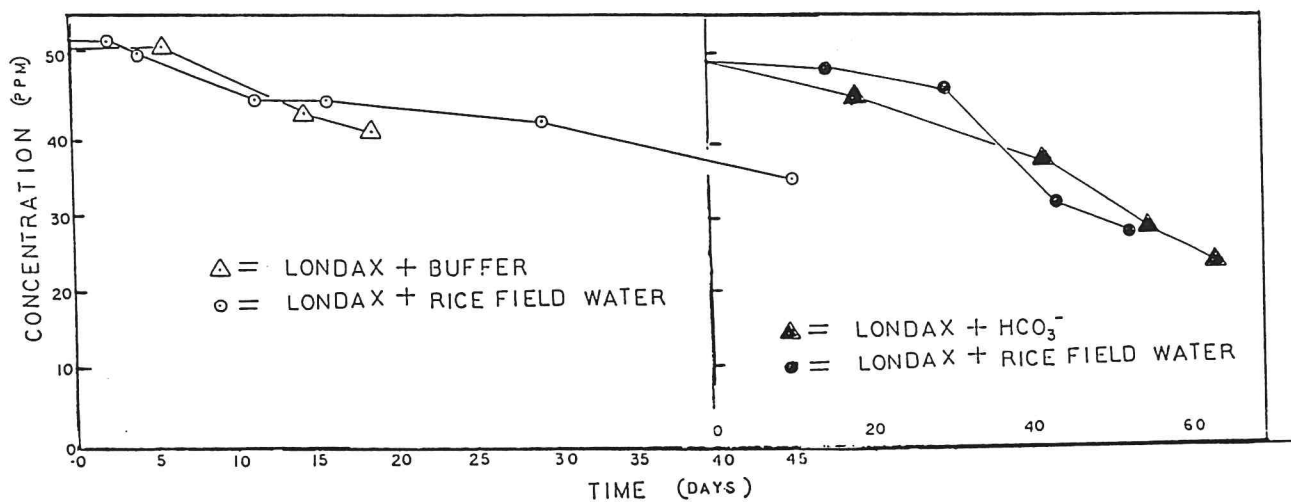


Fig. 2. Photolysis rates of Londax in pH 8.0 buffers and in rice field water.

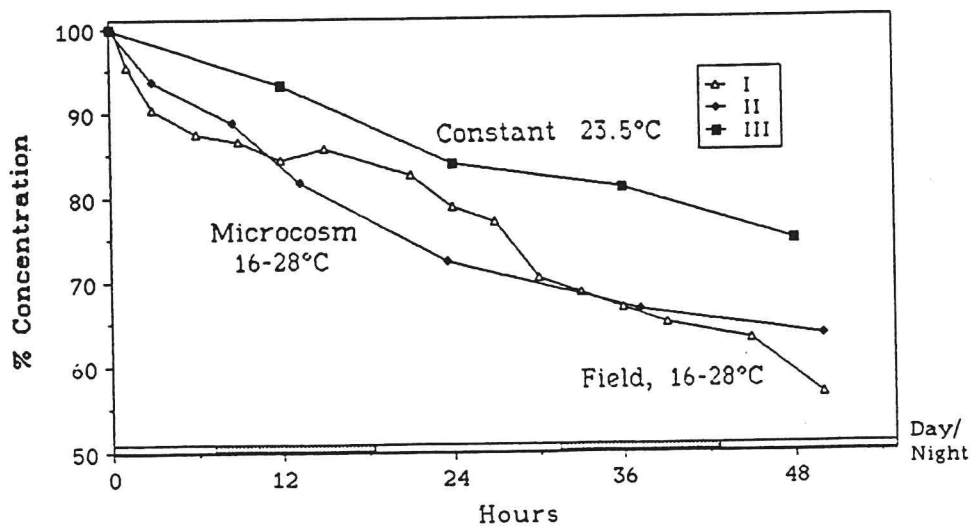
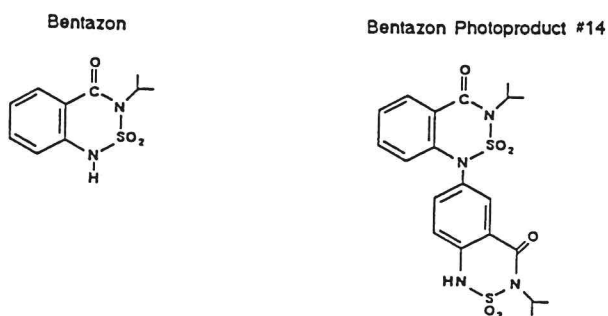


Fig. 3. Dissipation rates of bentazon in the microcosm and in field water.

Table 2. Field and microcosm experiments with bentazon.

Experiment	Profiles		Chemical Formulation	t _{1/2} (days)
	Temperature	UV		
I. Field	Field, 16-28°C	Field	Basagran [®]	2.90
II. Microcosm	Field, 16-28°C	Constant	bentazon	3.00
III. Microcosm	Constant, 23.5°C	Constant	bentazon	4.12
IV. Microcosm	Constant, 23.5°C	Field	bentazon	6.39

The UV absorption spectrum of bentazon in pH 8 water showed maxima at 338 nm and 376 nm -- well into the sunlight region -- compared to the published 302 nm maximum (measured in methanol), explaining its comparatively rapid outdoor photolysis. Bentazon photolysis in water proved to be complex; 16 products were isolated by a multistep HPLC procedure, 4 of which were formed without light and stable, two more which were unstable to light, 4 which were generated by light and stable, and 5 which formed in light but were later degraded. None of these was volatile enough for either gas chromatography or normal mass spectrometric analysis, and only one major photoproduct has been identified (structure shown below) despite an extensive effort. However, for monitoring the photoproducts, a 1-step HPLC procedure has been devised.



Investigation and modelling of bentazon's environmental fate is important. Unlike thiobencarb, which is dissipated primarily by volatilization and by adsorption to soil, bentazon is dissipated largely by photolysis and movement in water -- it is only weakly bound by soil and presumably could move through wet dikes. While a 9-day holding period would allow the loss of 90% of applied bentazon, it would generate several stable and nonvolatile photoproducts which would be released with the field water and whose identity and fate should be of concern.

Objective II.

1. Mass-balance field trial of ZnO-catalyzed degradation of thiobencarb. A mass-balance trial was conducted at the Scheidel

Ranch in Sutter Co. (Fig. 1, location 6). Six parallel basins of about 7 acres (2.8 ha) each were flooded and seeded as usual and then sprayed aerially with 4 lbs/acre (4.5 kg/ha) with Bolero 10G. After 6 days (24 May), the two center basins (C and D) were sprayed aerially with 10 lbs/acre (9 kg Zn/ha) of a suspension of high-grade (99.9+%) zinc oxide (ZnO), one lb/gal in water, starting about 11 a.m. in full sun; the adjacent basins (B and E) received 5 lbs/acre (4.5 kg Zn/ha), while the opposite end basins (A and F) were left untreated (controls). Samples of water and soil were collected at frequent intervals for analysis, and temperature, pH, and dissolved O_2 were monitored (Fig. 4); sample collection continued until 14 days after Bolero application.

Water samples were collected in a Teflon cup at a distance of three feet from shore, taking care to exclude sediment, passed through a $0.45\ \mu$ membrane filter, and frozen until analysis. Sediment was collected to a depth of 2.5 cm in a 16 cm-diameter plastic ring (area $2.01\ dm^2$), excess water drained off, and frozen. For water analysis, part of each sample was passed through a Bond-elut resin cartridge, the extracted organics eluted with ethyl acetate and concentrated, and thiobencarb determined by GLC with a nitrogen-phosphorus detector (sensitivity 1 ppb). Thiobencarb degradation products were determined by HPLC with a 254 nm UV detector (sensitivity 1 ppb). Frozen soil samples were thawed, air-dried, extracted with ethyl acetate, and analyzed for thiobencarb by GLC. Zinc in water and in soil was determined by ICP atomic absorption, sensitivity 10 ppb).

Thiobencarb concentrations in water for all six basins are shown in Fig. 5, and, for clarity, for one high-ZnO (C), low-ZnO (B), and control (F) treatment (Fig. 6). It appears that ZnO at both rates sharply reduced thiobencarb levels within several hours, and that the effects were dependent upon the amount of ZnO applied (Table 3). Relative % declines are more easily seen when graphed in relation to concentrations found in each basin just before ZnO treatment (Fig. 7). The controls (open symbols in Figures) obviously present a problem immediately following ZnO application; both show the sharp decline in thiobencarb concentrations expected of ZnO treatment. More careful examination reveals that the decline in control basin F did not occur until some hours later than in the others, and largely at night (Fig. 8), and the low dissolved-zinc levels in the control basins (Fig. 9) indicate that the decline probably was not due primarily to ZnO drift. We previously observed a similar sudden natural decline of residues in our 1984-85 field tests with molinate, but it remains unexplained.

As in our previous thiobencarb field tests (1985 Report), residue levels in the water rose slightly after their ZnO-induced decline due to continued desorption which partially offset thiobencarb losses by volatilization and photolysis (Fig 6). The soil data (Table 4) indicate no clear differences between the treatments, but the average thiobencarb level for the entire field declined with time. Although control basin F retained the highest residues in the water, its soil residues inexplicably were lowest.

Table 3. Effect of ZnO photocatalysis on thiobencarb in water (ppb)

<u>Basin</u>	<u>Before ZnO</u>	<u>After ZnO</u>	<u>Decline %</u>	<u>Residue at 94 h</u>	<u>Decline %</u>	<u>Residue at 191 h</u>	<u>Decline %</u>
A	159	96	40	59(118) ^a	63(26)	24(83)	85(48)
B	183	113	39	76	59	32	83
C	214	92	57	72	67	28	87
D	180	133	26	86	52	39	78
E	189	117	38	68	64	37	80
F	265	274	-3	121(182)	54(31)	63(122)	76(54)

^a Values in parentheses are estimated (Fig. 8).

Table 4. Thiobencarb Residues in Soil and Water.

<u>Time hrs</u>	<u>Soil ppb</u>	<u>Water ppb</u>	<u>Soil/ Water</u>	<u>Soil ppb</u>	<u>Water ppb</u>	<u>Soil/ Water</u>	<u>Soil Aver.</u>
Control Basin A				Control Basin F			
-16	2510	158	15.9	1990	269	7.4	2250
22	2800	94	29.8	1550	186	8.3	2180
46	2170	86	25.2	1680	168	10.0	1930
94	1890	59	32.0	1990	121	16.4	1940
191	2070	24	86.3	1740	63	27.6	1910
Low Basin B				Low Basin E			
-16	2030	241	81.4	1380	184	7.5	1710
22	3190	114	28.0	2510	127	19.8	2850
46	2630	86	30.6	3130	95	32.9	2880
94	2330	76	30.7	2390	68	35.1	2360
191	2050	32	64.1	1420	37	38.4	1730
High Basin C				High Basin D			
-16	1350	165	8.2	1680	250	6.7	1520
22	1940	123	15.8	2810	119	23.6	2380
46	2070	100	20.7	2720	99	27.5	2400
94	2420	72	33.6	2270	86	26.4	2350
191	1620	28	57.9	1980	39	50.8	1800
Soil Average (All Basins)							
-16	1820						
22	2470						
46	2400						
94	2210						
191	1810						

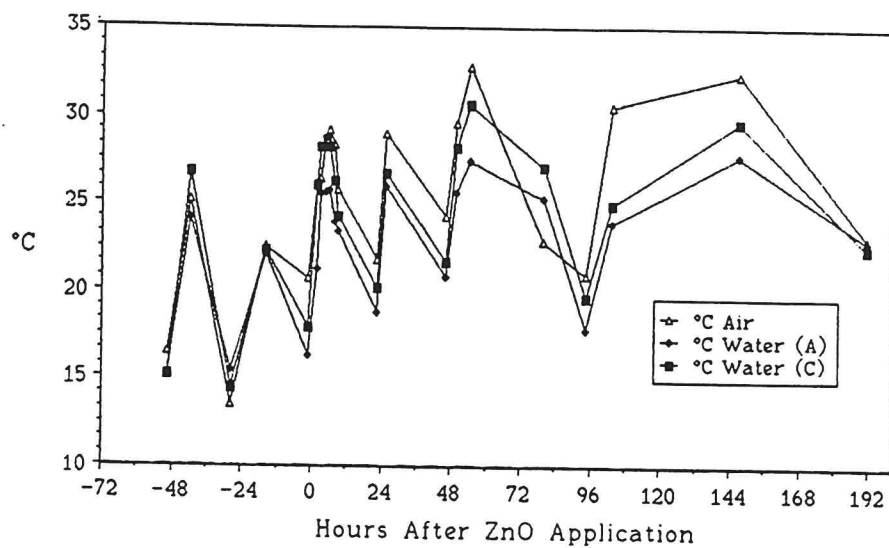


Fig. 4. Temperature variation in Scheidel Ranch basins.

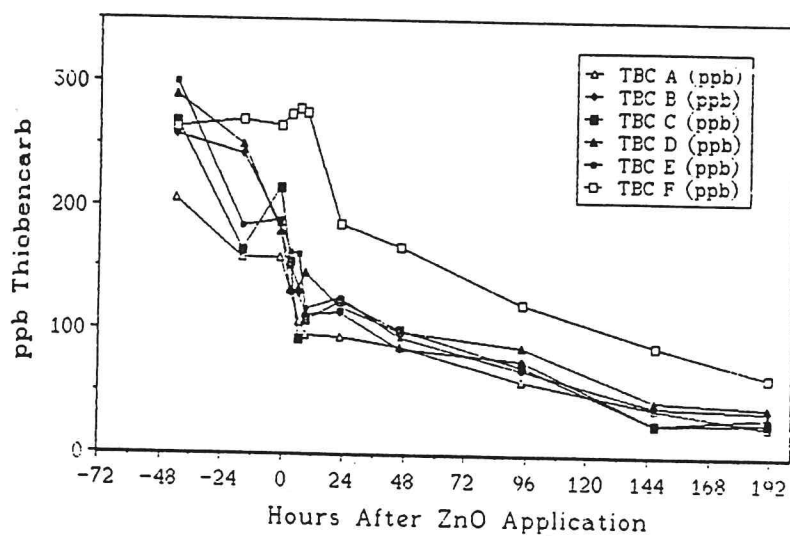


Fig. 5. Thiobencarb dissipation rates in water, with and without ZnO treatment. Basins A and F (open symbols), are untreated controls; B and E, 5 lbs/acre ZnO, C and D, 10 lbs/acre ZnO.

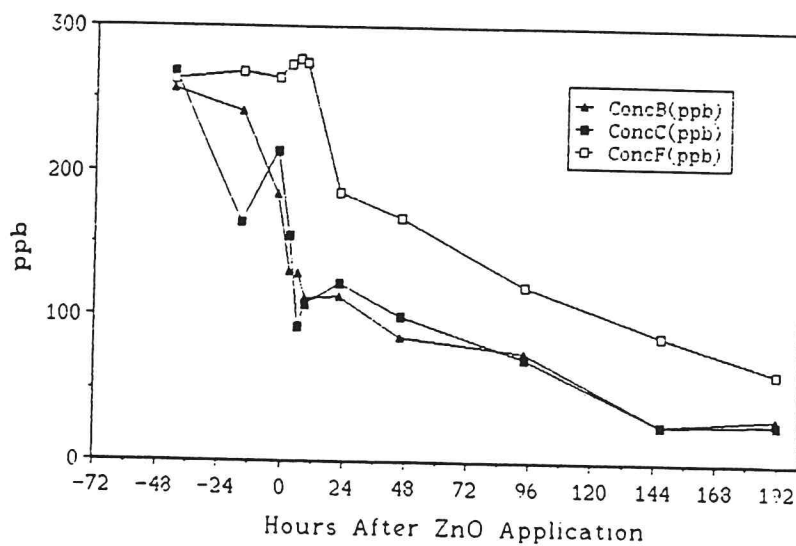


Fig. 6. Thiobencarb dissipation rates basins B, C, and F.

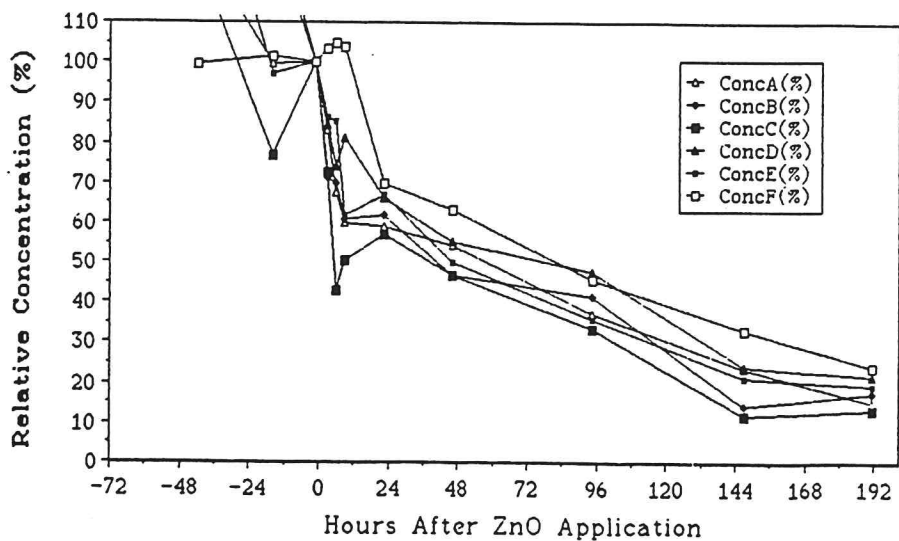


Fig. 7. Thiobencarb dissipation rates relative to pre-ZnO concentrations.

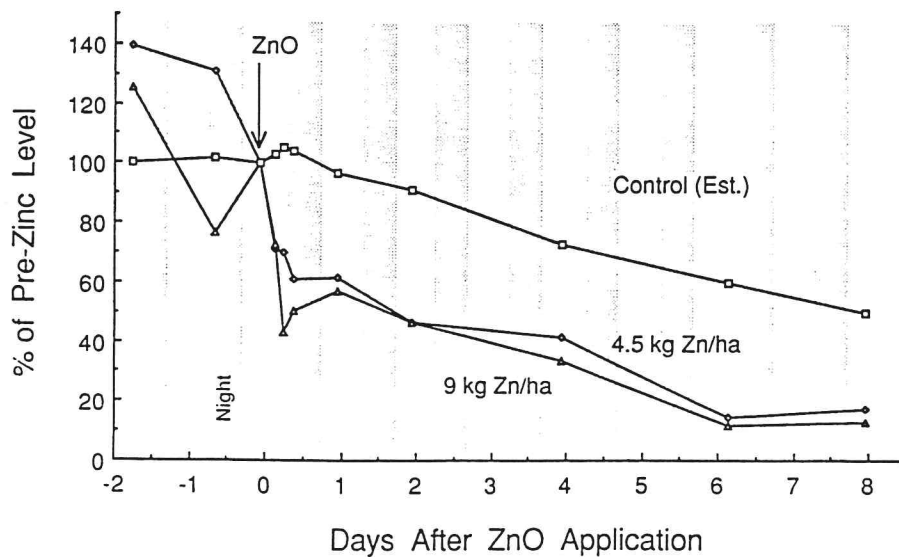


Fig. 8. Effect of ZnO on thiobencarb dissipation relative to estimated controls.

If one neglects the unexplained sudden drop in Control values and considers that dissipation should continue in them from hour zero according to the normal dissipation curve later observed (Estimated Control, Fig. 8), ZnO treatment produces a favorable result. The residue falls to 28 ppb (Basin C) after 191 hours (14 days after thiobencarb application) instead of the control's estimated 122 ppb (Table 3), for an almost 80% residue reduction. At 94 hours (10 days after thiobencarb application), the residue in Basin C was 72 ppb compared to the estimated 182 ppb in Control Basin F -- a 60% reduction, but still quite high.

However, in the actual field results as observed, the 87% residue reduction in basin C after 192 hours must be compared with reductions of 85% and 76% in Control Basins A and F, respectively (Table 3) -- an insignificant difference. The dissolved zinc levels (Fig. 9, Table 5) were roughly proportional to ZnO application rate, although Control levels were increased consistent with a small amount of ZnO drift. (Most zinc levels approached control values within 4 days, the highest requiring 6 days.) The principal photo-oxidation product, thiobencarb sulfoxide, was present in all basins prior to ZnO treatment (Fig. 10) and, closely paralleling the parent, declined sharply on Day 0; other photolysis products -- p-chlorobenzaldehyde and p-chlorobenzoic acid -- were detected only sporadically at the low ppb range.

Table 5. Dissolved zinc levels (Mass-balance Study) (ppb).

Time (hrs/days)	Basin A	B	C	D	E	F
-16/-0.7	13	10	6	6	9	4
0.0/0.0	--	ZnO	ZnO	ZnO	ZnO	--
22/0.9	32	622	437	1021	225	26
46/1.9	25	270	243	570	193	12
94/3.9	25	50	47	172	36	5
146/6.1	3	8	5	22	10	7
191/8.0	3	6	6	24	5	3

Thiobencarb levels in bottom sediments did not change radically upon ZnO application at 0 hours (Table 4). Note that these values are in the ppm range, whereas those in water are still in ppb; a typical 40% decline of thiobencarb in water represents only 2% of the soil level (that is, 0.04 ppm) and usually would be lost in the variability between the duplicate soil samples. Only two trends were observed: soil levels of thiobencarb generally were still increasing at the time of ZnO treatment (6 days after herbicide application), but the average level for the entire field (6 basins) and for each separate treatment then gradually declined with time (as it should) from a maximum of 2.5 ppm to 1.8 ppm within 8 days. The soil-water ratios, initially close to the 7.5 figure found by others, increased substantially with time, indicative of

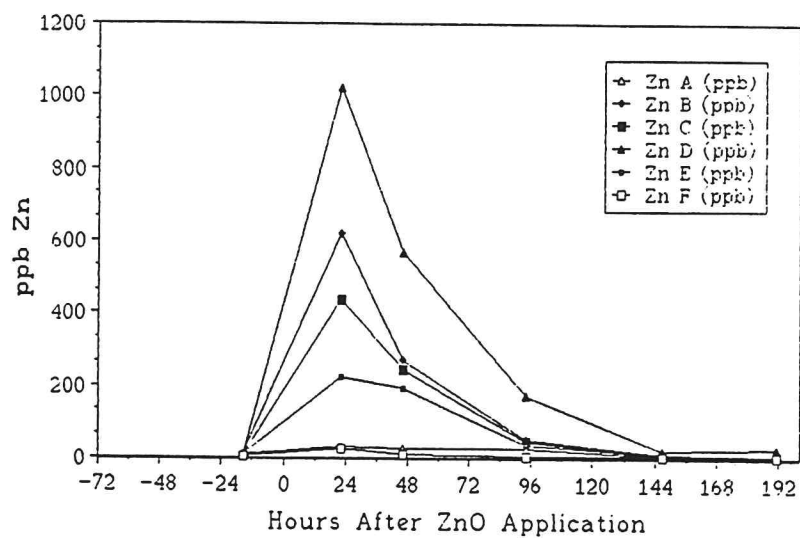


Fig. 9. Zinc concentrations in water in relation to ZnO application.

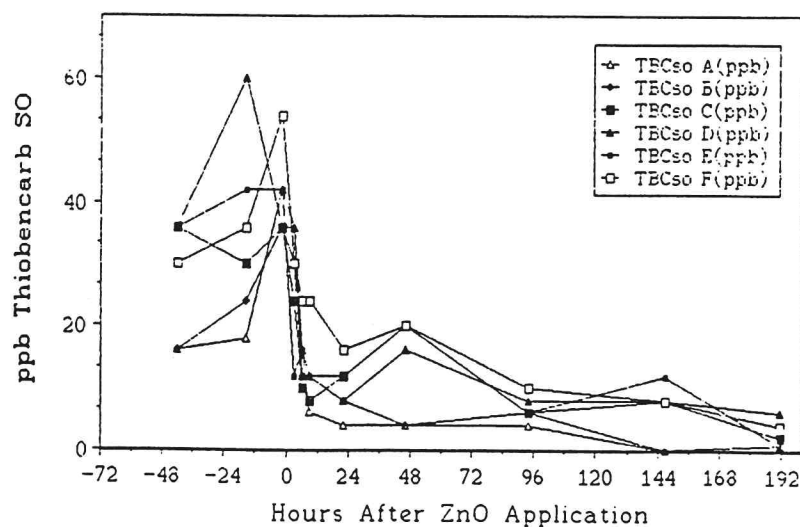


Fig. 10. Thiobencarb sulfoxide (TBC_{SO}) concentrations in field water.

thiobencarb's tendency to bind to soil. Although concentrations in water generally were in the low ppb range after 191 hours (14 days after herbicide application), concentrations remained relatively high on soil particles which, suspended and moving in water, provide a continuing reservoir.

Both the soil and water values were well below those expected from our previous work and from that of the California Department of Food and Agriculture. Typical concentrations in water (in 9 of 10 experiments) had been found to fall between 400 and 800 ppb at Day 6, whereas those of the present work were between roughly 100 and 200 ppb. Likewise, typical earlier soil concentrations of 3.9 ppm (dry weight) must be compared with the present average of 1.8-2.5 ppm. Again, it appears that ours was not a typical field situation, with 6-day thiobencarb concentrations resembling those more often seen at 12-14 days after herbicide treatment; probably, less than 4 lbs/acre of Bolero was applied.

We conclude that a combination of circumstances -- probably the natural variation in field residues and sampling plus some photo-oxidation from ZnO drift -- resulted in the confusing Control values. From previous experience and the full-scale 1986 field experiments (Section III), we assume that ZnO-catalyzed photolysis had some part in the decline of the Scheidel Ranch residues, but clear scientific evidence is lacking.

2. Toxicity of zinc to rice field organisms. One of the concerns over possible field use of ZnO is that the increased zinc levels might harm fish and wildlife. As an initial test, a fish species (Gambusia affinis), a mollusc (pond snail, Helisoma tenue), an arthropod (tadpole shrimp, Triops longicaudatus), and amphibian larvae (bullfrog, Rana catesbiana) were caged in plastic containers and placed in Basins A, C, and E during the mass-balance experiment. The tadpole shrimp were caged separately from the others, to avoid eating by the fish. The animals were acclimated and observed both before ZnO application under (thiobencarb exposure only) and repeatedly for 96 hours afterward. Thirty of each species were used in each basin.

Results are summarized in Fig. 11. Neither thiobencarb alone nor the combinations of thiobencarb and Zn had any significant effect within 48 hours on any of the organisms, despite the increasing temperatures which developed in the stagnant water (Fig. 4). Although several animals escaped through a loose lid or were cannibalized, none were ever observed moribund or dead. The test was abandoned at 96 hours when low water levels and elevated water temperatures caused obvious stress.

In the laboratory, accurate determinations were made of the median lethal doses of dissolved zinc for Gambusia and Triops in a flowthrough test system; details of the system are available but not included here. Groups of 6 animals were exposed to each of 9 concentrations of ZnSO_4 in tap water at 25°C; the Triops were housed individually to avoid cannibalism. Mortalities were determined at

24, 48, 72, and 96 hours with fish, but only at 12 and 24 hours with Triops, as the animals could not survive longer than 2 days without food.

The results are shown in Fig. 12 and Table 6. while the standard 96-hours LC_{50} for Gambusia was 15.0 ppm, the field concentration of Zn^{++} exceeded 1 ppm only within the first 24 hours; the 24-hour LC_{50} was 21.7 ppm. Tadpole shrimp were much more sensitive to Zn^{++} , the 24-hour LC_{50} being only 0.46 ppm and the 12-hour LC_{50} being 1.25 ppm. However, the field test indicated that they could survive the first hours of elevated Zn levels. None of these tests confronted the question of effects on newly hatched animals or possible long-term responses to the briefly-elevated zinc levels, but the extensive literature on zinc toxicity indicates that the effects of nonlethal exposure are completely reversible in aquatic animals.

Table 6. Toxicity of $ZnSO_4$ to Aquatic Animals^{a,b}

	<u>Gambusia affinis</u> (Mosquitofish)	<u>Triops longicaudatus</u> (Tadpole shrimp)
Length, mm (range)	25.8 (19.5-32.2)	5.4 (3.1-8.6)
Weight, mg (range)	176.8 (124.8-245.6)	---
LC_{50} , 12 hr	--	1.25 (0.73-2.11) ^c
LC_{50} , 24 hr	21.68 (19.09-24.74) ^c	0.46 (0.17-0.63) ^c
LC_{50} , 48 hr	17.76 (15.30-21.25) ^c	--
LC_{50} , 72 hr	16.29 (13.76-19.23) ^c	--
LC_{50} , 96 hr	14.99 (12.44-17.39) ^c	--

^a pH 7.00, DO > 4 mg/L, T°C = 25, flow 5 mL/min, n = 6.

^b LC_{50} in ppm (mg Zn/L).

^c 95% Confidence limits.

3. Persistence and degradation of fenoxaprop-ethyl (Whip®). The 1985 photolysis studies showed the rapid degradation of fenoxaprop-ethyl; half-lives of 44 and 14 hours were observed in distilled and field water, respectively, in the laboratory. Some degradation also occurred in the dark. To help determine the role of hydrolysis and microbial metabolism in this degradation, solutions of fenoxaprop-ethyl in buffered distilled water, sterile and nonsterile, were irradiated in a photoreactor, samples taken at regular intervals, concentrated on C-8 cartridges, and analyzed by gas chromatography. In sterile distilled water at pH 6.4, previously shown not to cause hydrolysis of fenoxaprop-ethyl, the half-life was extended to 276 hours in the light, with no degradation in the dark (Fig. 13). In water that was buffered but not sterilized, the half-life still was 101 hours in the light and 165 hours in the dark; in buffered field water, the rates of degradation were much faster ($t_{1/2}$ 38 hours in light, 73 in dark). Thus, it appears that photolysis is not the only factor in the degradation of this herbicide, but, in combination with other environmental forces, it results in the very rapid degradation of fenoxaprop-ethyl observed before.

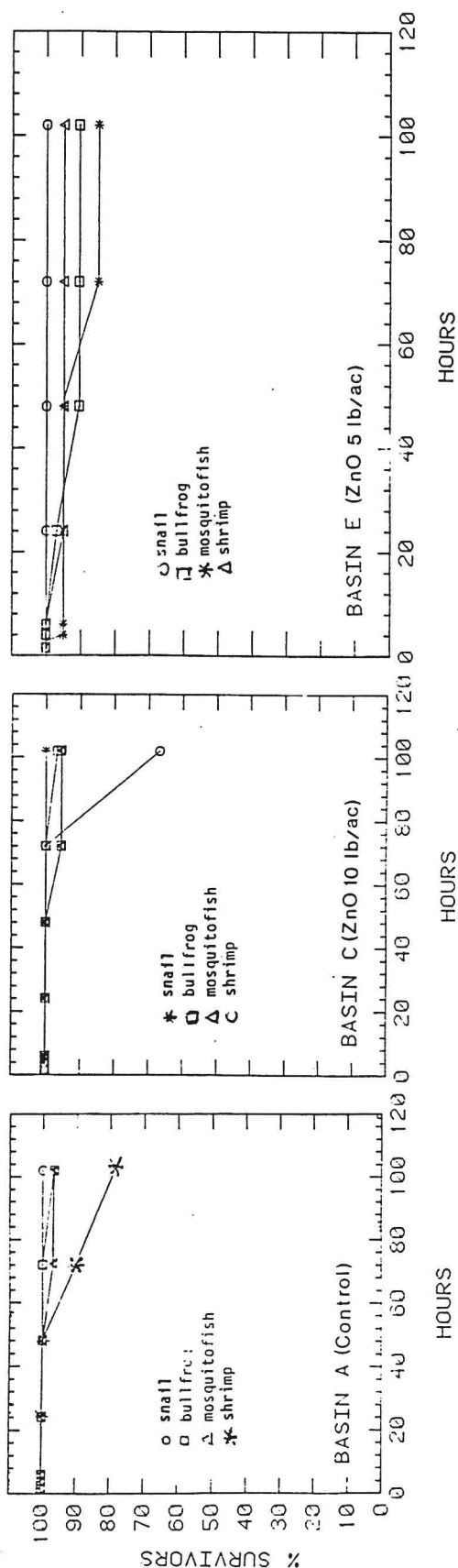


Fig. 11. Field toxicity tests in fish (Gambusia), bullfrog tadpoles (Rana), snails (Helisoma), and tadpole shrimp (Triops) after ZnO treatment. Number of each species = 30.

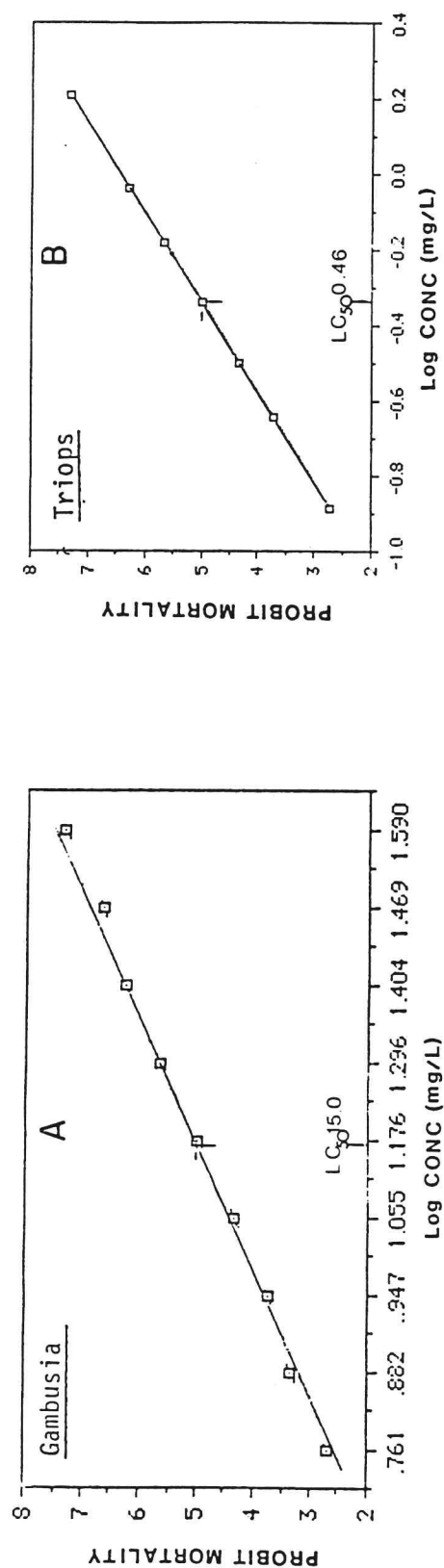


Fig. 12. Toxicity of dissolved zinc (A) to fish (Gambusia) and (B) to tadpole shrimp (Triops). Each data point represents 18 animals in 3 replicates.

To investigate the products formed from fenoxaprop-ethyl under light and dark conditions, a solution of the chemical in distilled water was divided into two portions, put into sealed Pyrex bottles, and set outside in the sun during mid-July. One bottle was covered with aluminum foil to prevent exposure to sunlight. Samples were taken at regular intervals, concentrated, and analyzed by gas chromatography/mass spectrometry (GCMS) and by HPLC. In the dark, the major products were fenoxaprop acid, 6-chlorobenzoxazolinone, 4-hydroxyphenoxypropionic acid, and one unidentified product. Of the four, only 6-chlorobenzoxazolinone was detected in the light, the others presumably being photolyzed to simpler products. Mass spectral evidence suggested the presence of ethyl 4-hydroxyphenoxypropionate in the irradiated solution, and small amounts of three other unidentified products were observed by HPLC.

Rates of degradation also were studied on soil surfaces. Sandy loam from a rice field near Davis was sifted through a 0.124 mm screen, slurried with water, and spread evenly on glass plates covered with filter paper. Equal amounts of fenoxapropethyl were sprayed on each plate, and half of them were allowed to dry while the remainder were kept wet by a reservoir of buffered water in contact with the filter paper. The plates were then placed outside where one half of each group was exposed to early August sunlight, while the other half was kept covered. The results are summarized in Fig. 14. In both dry and wet soil, degradation was observed in the dark, which again suggested possible microbial breakdown; repeated attempts to keep the soil sterile were unsuccessful. In both cases, degradation was accelerated by light, resulting in an 80% loss of the compound within 11 days on wet soil and 4 days on dry.

The soil adsorption coefficient (K_d), the ratio of the concentration of a chemical in soil to that in water at equilibrium, indicates how an herbicide will partition between soil and water when applied to a flooded field. The K_d for fenoxaprop-ethyl was determined by shaking flasks containing soil, water, and herbicide for 12 hours and then measuring the concentration in the two phases. Using sandy clay typical of California rice fields, a K_d value of 53 (μg per gm soil/ μg per mL in water) was obtained, showing fenoxaprop-ethyl to be bound moderately.

Another field study, with more intensive sampling than that done previously, was completed this year at the Scheidel Ranch. Whip[®] was sprayed into 4.5 m² rings set in a flooded rice field and also applied to an adjacent drained field. Water and soil samples were taken at regular intervals, extracted, analyzed by GC, and the results compared with those of 1985. Fenoxaprop-ethyl was dissipated very quickly from field water, with half-lives consistently less than 3.5 hours (Fig. 15). Soil concentrations in the flooded field dropped more slowly, from almost 700 ppb at 10 hours after spraying to below detection (20 ppb) within 50 hours. In the field drained before spraying, 9000 ppb were detected initially, with 75 ppb of fenoxaprop-ethyl still detectable after 136 hours.

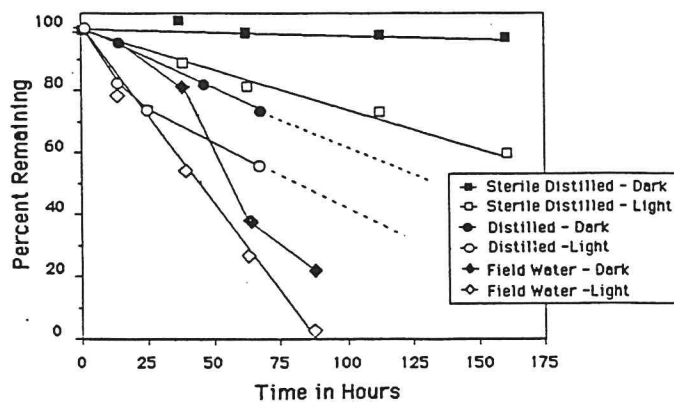


Fig. 13. Fenoxaprop-ethyl dissipation rates in water.

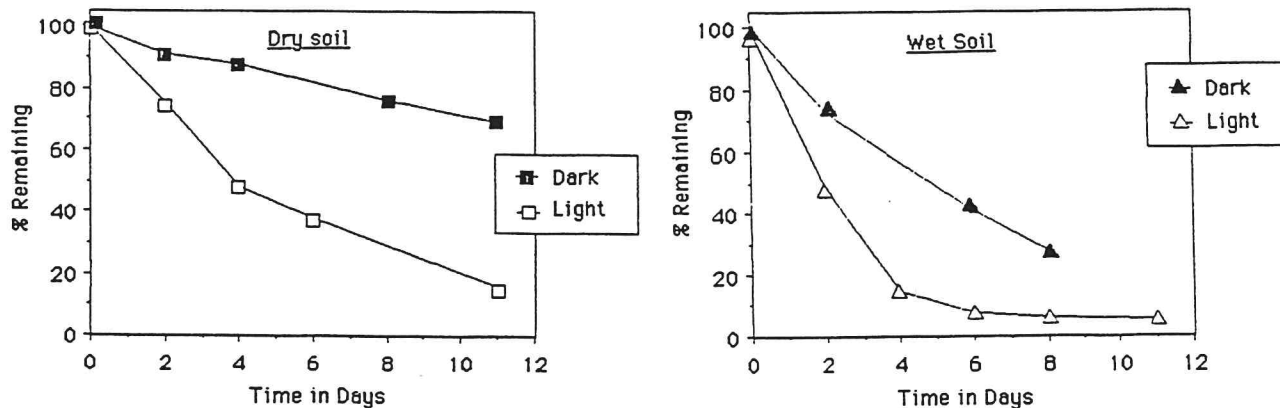


Fig. 14. Fenoxaprop-ethyl dissipation rates on dry and wet soil.

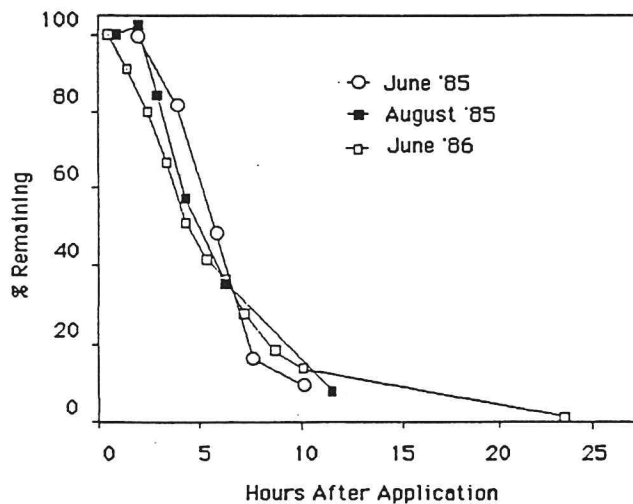


Fig. 15. Fenoxaprop-ethyl dissipation rates in field water at three locations.

The combined results from experiments in the lab and field during 1985 and 1986 suggest that Whip herbicide is not persistent in either water or soil under California ricefield conditions. Soil adsorption contributes to its dissipation from water, and the processes of hydrolysis, microbial metabolism, and photolysis all contribute to rapid degradation.

4. Molinate metabolism in fish. Of the fish species exposed to molinate in Sacramento Valley drains and rivers, the common carp is the principal one involved in the much-publicized "fish-kills". It was of interest to learn the reasons for this seeming specificity, both with the aim of protecting local fish, if possible, and to examine the use of such thiolcarbamates for intentional destruction of carp in other parts of the country where they are considered "trash fish".

The flow-through system described previously provided adequate aeration and a low-stress environment, ^{14}C loss through volatilization was minimal, and microbial breakdown was not detected. Compared to isocratic HPLC analysis, gradient-elution minimized peak broadening, tailing, and analysis time; amounts as small as 0.3 nmol could be detected accurately and reproducibly.

Bioaccumulation was rapid but not excessive; the bioconcentration factors (BCFs) were 25.26 for striped bass, 19.72 for white sturgeon, and 30.48 for common carp, but differences between the BCFs were not significant ($P > 0.05$). In general, 24-hour depuration by all three species was extensive, but depuration by common carp (77.81%) was significantly slower than that by either striped bass (90.47%; $P < 0.01$) or white sturgeon (95.98%; $P < 0.01$). All three species oxidized molinate to a number of products, and both hydrolyzed and conjugated the sulfoxide or sulfone (Table 7). Both white sturgeon and common carp also conjugated 4-hydroxymolinate with glucuronic acid, forming the β -D-glucuronide.

In mammals, thiocarbamate sulfoxidation followed by glutathione (GSH) conjugation is considered a detoxication pathway. Sulfoxidation produces better carbamylating agents, which are then susceptible to further GSH deactivation. When combined, production of molinate sulfoxide and the mercapturic acid by common carp (1.22% of total ^{14}C) was significantly lower than that by striped bass (13.40%; $P < 0.05$) or white sturgeon (7.88%; $P < 0.01$). Overall, the selective toxicity appears due to a combination of increased bioconcentration, decreased depuration, and decreased detoxication by common carp.

Tables 7. Molinate metabolite profiles for three species of fish.

¹⁴ C disposition								
Component	Striped bass			White Sturgeon			Common carp	
	nmol/g	a,b	%	nmol/g	a,b	%	nmol/g	a,b %
Molinate	12.98(1.89)		81.51	10.02(3.93)		69.87	15.62(3.47)	83.01
4-Hydroxymolinate	0.11(0.05)		0.69	1.00(0.74)		6.97	1.22(0.08)	6.48
Molinate sulfoxide	2.09(1.54)		13.13	0.56(0.17)		3.91	0.140(0.056)	0.74
4-Ketomolinate	0.020(0.010)		0.13	0.16(0.11)		1.12	0.31(0.05)	1.65
Carboxymolinate	0.66(0.21)		4.14	0.36(0.12)		2.51	0.62(0.09)	3.29
Hexhydroazepine	0.020(0.002)		0.13	0.42(0.26)		2.93	0.27(0.08)	1.43
Molinate mercapturic acid	0.043(0.006)		0.27	0.57(0.10)		3.97	0.090(0.026)	0.48
4-Hydroxymolinate-β-D-glucuronide	ND ^c	---	---	1.25(0.32)		8.72	0.55(0.25)	2.92
Totals	15.92(2.13)		100.00	14.34(4.57)		100.00	18.82(3.31)	100.00

^a Mean (SD); N=3.

^b Wet weight.

^c None detected.

C. Objective III.

1. Field trials on effects of ZnO on thiobencarb residues in water. As a practical test of the efficacy of ZnO photocatalysis for reducing thiobencarb residues in flooded rice fields, five commercial fields in addition to the Scheidel Ranch were selected to represent the three major soil types of the Sacramento Valley (Fig. 1, Table 8). The fields were flooded, seeded, and treated with 4 lbs/acre of Bolero 10G as usual. After variable holding periods during which weed control was effected (Table 8, Column 7), as judged by the grower and farm advisor, high-purity zinc oxide was aerially applied at a rate of 10 lbs/acre (9 kg Zn/ha) as a 1 lb/gal aqueous spray. Adjacent control fields were left untreated. Water and sediment were sampled regularly (duplicates) from before ZnO treatment to 14 days following Bolero application.

Results are summarized in Table 8 and Fig. 16. Analytical results tended to be quite erratic, as the fields were maintained with normally varying water depth and new water added, and a wide range of thiobencarb concentrations was encountered at the time of ZnO treatment (Column 8). No ZnO-treated field failed to respond (Column 10), with residue declines approaching 60%, although in Field 5 as at Scheidel Ranch, the control field showed a major drop in thiobencarb level at the same time. However, by the end of the required 14-day Bolero holding period, thiobencarb residues often still exceeded 100 ppb (Column 11), and ZnO usually had afforded little advantage over natural dissipation at that time (Column 12). Dissolved zinc exceeded a maximum of 1 ppm in only two instances (Column 13), but because of the short dissipation time before water would be released, levels generally had not returned to their pre-ZnO average of 8 ppb (Column 14).

While the tests were not an unqualified success, they were typical of what is to be expected. In fields with high thiobencarb residues, especially those for which the decision to reduce herbicide levels was made at an early time (about 6 days), ZnO application allowed an immediate 60% reduction (Fields 3 and 6) with dissolved zinc residues low enough to allow safe release of water within three days. As the herbicide holding-period got longer and the residues smaller (Field 5), use of ZnO was increasingly less advantageous, and zinc levels still remained high 14 days after Bolero application. As expected, a higher rate of ZnO produced better results under these circumstances (Field 2), but also resulted in higher dissolved zinc residues. Clouds, too, may have affected the results, even with early ZnO treatment (Field 3).

ZnO works, but not to equal advantage under all conditions.

Table 8. Characteristics of Commercial Thiobencarb (TBC) Test Fields.^a

1	2	3	4	5	6	7	8	9	10	11	12	13	14
No.	Owner	County	Soil	Acres	Bolero Applied	Days to Zn0	TBC Day 0	TBC Day 1	Loss %	TBC at end	Loss %	Zn max	Zn at end
1	LeGrand	Colusa	Willows	41.7	4/13	8	420	200	52	154	63	519	100
1C	"	"	"	82.3	--	--	390	346	11	186	52	73	4
3	Dennis	Colusa	Willows	26.6	4/24	6	320 ^b	216	33	105	67	266	4
3C	"	"	"	32.8	--	--	180	183	-2	116	36	17	<13
4	Tennis	Butte	Stockton	34	4/24	9	362	305	16	187	48	143	42
4C	"	"	"	51	--	--	313	478	-53 ^c	217	31	39	6
5	Boerger	Butte	Stockton	51	4/22	11	98	74	24	47	52	1179	329
2	Dubois	Sacto	Sacto	51	4/19	9	337	123	64	74	78	1137	204
2C	"	"	"	51	--	--	250	229	8	33	87	53	21
6	Scheidel	Sutter	Sacto	14	4/19	6	197	112	57	82	58	729	15
6C	"	"	"	7	--	--	265	274	-3	63	76	26	3

^a Residues are in ppb (µg/L).^b High clouds.^c Field almost dry.

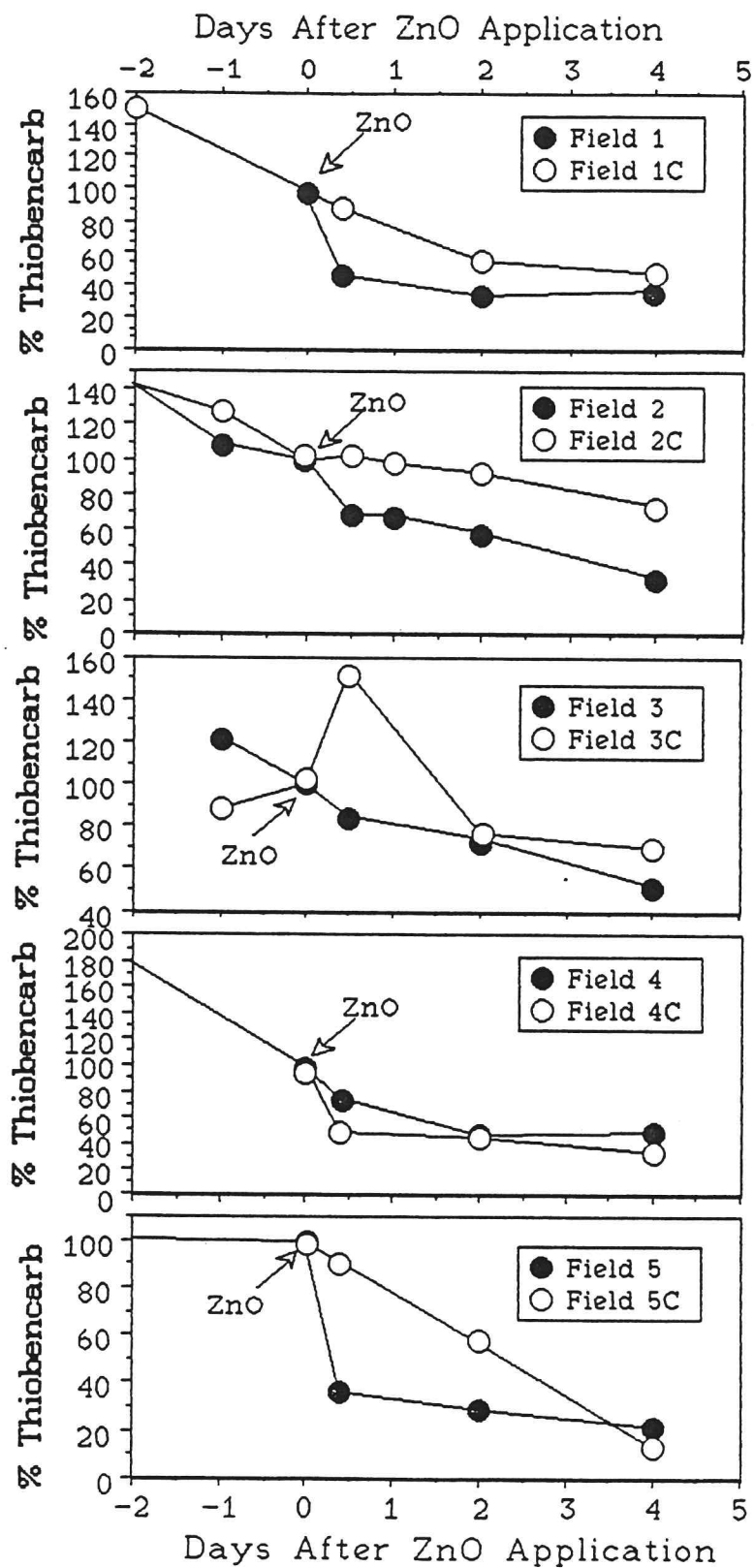


Fig. 16. Effect of ZnO on Thiobencarb levels in field water at 5 Sacramento Valley locations. (See Table 8).

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- M.B. Freiberg and D.G. Crosby. 1986. Loss of MCPA from simulated spray droplets. J. Agr. Food Chem. 34:92-95.
- J.L. Benoit-Guyod, J.B. Bowers and D.G. Crosby. 1986. Degradation of MCPA by ozone and light. Water Research 20:67-72.
- D.G. Crosby, R.B. Draper and R.M. Higashi. 1986. Enhanced photo-oxidation of rice herbicides. J. Agr. Food Chem., in press.
- D.G. Crosby, R.B. Draper and R.M. Higashi. 1986. Enhanced photo-oxidation of rice pesticides. Sixth Internat. Congress of Pesticide Chem., Toronto, Paper 6A-12.
- R.M. Higashi and D.G. Crosby. 1986. A physical-chemical microcosm for ricefield environmental fate studies. Sixth Internat. Congress of Pesticide Chem., Toronto, Paper 6D/E-13.

CONCISE GENERAL SUMMARY OF CURRENT YEAR'S RESULTS:

In support of possible field use of semiconductor photocatalysts to reduce pesticide residues in water, sunlight intensity was found to affect herbicide degradation proportionate to intensity, but that some haziness or high clouds could be tolerated. The degradation also was inhibited by acidic conditions, but a field survey showed Sacramento Valley water generally to be alkaline except along the east side. It was found that zinc oxide (ZnO) slurry could be sprayed successfully at concentrations up to 1 lb/gal, so a mass-balance field trial was conducted on the effect of ZnO on thiobencarb persistence. Under normal growing conditions, ZnO applied at 10 lbs/acre six days after Bolero application reduced herbicide levels up to 57% in water to about 100 ppb, although controls also showed unexplained reductions. Because of thiobencarb's soil adsorption, its levels in sediment remained at 10-30 times those in water after ZnO treatment and only slowly declined with time. Thus, sediment continued to provide a reservoir of herbicide even after release of the water. Dissolved zinc seldom exceeded 1 ppm, although it often did not return to pre-ZnO levels within the holding period. Caged ricefield fish, snails, frogs, and tadpole shrimp appeared unaffected during the experiment. Laboratory tests with dissolved zinc showed a 24-hour median lethal dose (LC₅₀) for mosquito fish of 21.7 ppm and a 96-hour LC₅₀ of 15.0 ppm, but tadpole shrimp were much more sensitive (12-hour LC₅₀ 1.25 ppm, 24-hour LC₅₀ 0.46 ppm).

Five full-scale tests were conducted on fields representing the three major Sacramento Valley soil types. Despite erratic behavior, residues again were reduced immediately up to about 60%; by holding the water for the required 14 days, most advantage was lost at the end, due to natural dissipation. Dissolved zinc levels seldom exceeded 1 ppm, but residues again had not always returned to pre-ZnO levels within the holding period. If the decision to use ZnO was made within about 6 days after Bolero application, residue reduction was effective without excessive zinc remaining; as the holding time increased, ZnO treatment became increasingly less advantageous. Higher rates were more effective but also led to greater persistence of dissolved zinc.

Other herbicides, with more attractive persistence characteristics, were investigated. Bentazon (Basagran), whose field dissipation was successfully modelled in the laboratory microcosm, was readily degraded by sunlight (field

half-life 2.9 days) and non-volatile, but it was only weakly bound by soil and formed several persistent and complex photoproducts. Fenoxaprop-ethyl (Whip[®]) also was degraded readily to identified, nonpersistent fragments under field conditions (half-life > 4 hours) by a combination of microbial action and sunlight, and it proved to be moderately adsorbed to soil; its persistence characteristics look very good. Londax remained almost unchanged by either sunlight or microorganisms, yet it disappeared rapidly from water during field tests and was assumed to bind quickly and tightly to soil -- possibly advantageous and worth more investigation. It seems likely that development of such herbicides could allow the eventual replacement of the more troublesome ones now in use.