

COMPREHENSIVE RESEARCH ON RICE  
ANNUAL REPORT  
January 1, 1984 - December 31, 1984

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: \$27,100

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. Effects of atmospheric ozone on chemicals in water (UC-Davis).
  2. Enhanced photo-oxidation: Laboratory comparison of oxidants and conditions affecting zinc oxide oxidations (UC-Davis).
  3. Identification of enhanced photo-oxidation products (UC-Davis).
  4. Ricefield microcosm: Formulation properties vs. field dissipation (UC-Davis).
  5. New method for analysis of organic solutes in water (UC-Davis).
  6. Laboratory purification and photodegradation of Londax in water (UC-Davis).
- B. Objective II. To estimate the relative importance of such factors to the practical use of specific rice pesticides.
1. Concentrations of atmospheric ozone over rice fields (UC-Davis, Sacramento County, Colusa County).
  2. Sampling and analysis of molinate field residues (UC-Davis, Colusa County).

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

1. Comparative molinate analyses (UC-Davis).
2. Enhanced photo-oxidation: Field experiments (Rice Experiment Station, Biggs; Rice Research Facility, Davis; UC-Davis).
3. Rice pesticide data bank (UC-Davis).

**SUMMARY OF 1984 RESEARCH (MAJOR ACCOMPLISHMENTS) BY OBJECTIVE:**

**A. Objective I.**

1. Effect of Atmospheric Ozone on Rice Pesticides. Our previous reports have described the surprising photo-oxidizing power of ricefield water in pesticide degradation and the apparent importance of hydroxyl radicals (HO) in this process. Atmospheric ozone is itself a strong oxidizing agent in direct reactions with many other chemicals, but it also acts indirectly by generating HO both by photochemical reaction with water and by a nonphotochemical reaction with hydroxide ion. In order to explain the observed field oxidizing power and seek alternate sources of pesticide-destroying HO (other than the previously-described hydrogen peroxide), we have investigated for the first time the influence of atmospheric ozone on pesticides and other organic chemicals dissolved in water.

The newly-designed test chamber described in our 1983 report provided atmospheric ozone, at ambient as well as higher levels, uniformly to the surface of aqueous solutions of test chemicals. Ozone penetration, as measured by the bleaching of intensely-colored indigotrisulfonate dye, was close to that reported in outdoor field studies (0.3 mole/acre/day). Test chemicals represented a range of structural types and expected reactivities: the dye; the herbicides thiobencarb and CDAA; 2,4-dichlorophenol and p-nitrophenol as relatively persistent primary degradation products of 2,4-D and parathions; and the normally unreactive nitrobenzene.

All of the test compounds were degraded to some extent in distilled water, at rates depending upon  $O_3$  concentration and the presence of UV light, and the results indicated that both the direct and indirect reactions occurred. In order to determine the HO contribution, suitable chemical reagents were found (tetrachlorocyclohexanol and 3-bromopropanol) which would detect HO specifically, and its photochemical generation could be measured by the rate of loss of reagent (Fig. 1).

Contrary to the results in distilled water, test compounds and reagents reacted only slowly, if at all, in filter-sterilized field water. Effects of HO generated photochemically from  $O_3$  were masked by more rapid reactions with natural carbonates in the water, and the availability of HO generated by alkaline decomposition of dissolved  $O_3$  was reduced to insignificance by competing natural organics, as well; indirect ozone reactions with ricefield pesticides seem to be

ruled out. However, since much of the 0.3 mole/acre/day of ozone flux actually is consumed in HO generation, only very slow direct reactions, typified by degradation of CDAA (Fig. 2), would be expected. The oxidizing power of ricefield water must arise from sources other than ozone.

2. Enhanced photooxidation: Lab experiments. Oxidative degradation of pesticides by natural photosensitizers and photooxidants present in rice field water can cause slow dissipation of many chemicals. Our goal has been to evaluate the feasibility of enhancing oxidant (especially HO) concentration in rice field water, intentionally speeding the degradation of molinate and thiobencarb. We surveyed photooxidants which might be used to supplement natural oxidants in rice field water, and this initial survey was reported in 1983. Evaluating these results, we advanced persulfate, hydrogen peroxide, hypochlorite, titanium dioxide ( $\text{TiO}_2$ ), and zinc oxide ( $\text{ZnO}$ ) through a series of experiments designed to determine interferences by components of rice field water while maximizing herbicide oxidative efficiency with respect to rate and cost. The first three were temporarily abandoned either because of interference which reduced the rate of oxidation, expense, or because they might present pollution problems themselves. Work has continued on the two semiconductor powders,  $\text{TiO}_2$  and  $\text{ZnO}$ .

A simple suspension of  $\text{ZnO}$  (5 mg/L) in rice field water spiked with 2 ppm of molinate and irradiated with summer sunlight while closed to evaporation provided a molinate half-life of only 1.8 hours (Fig. 3). In a similar experiment using  $\text{TiO}_2$  (100 mg/L), 20 times the amount of semiconductor provided essentially only the same half-life (1.7 hours). In addition,  $\text{TiO}_2$  is an inert substance which could accumulate in the field from year to year and perhaps interfere with future pesticide applications. The inherent instability of  $\text{ZnO}$  in light and water also made it more attractive as an additive to induce the photooxidation of molinate; as  $\text{ZnO}$  slowly dissolves in sunlight and rice field water, it forms zinc ion which becomes available for rice plant nutrition. As  $\text{ZnO}$  is stable at pH 6.5-9, sprayable, nontoxic, and relatively cheap, it emerged as the best candidate for a limited field trial (See Section III. 2).

The possible persistence of byproducts led us to investigate the products of semiconductor photooxidation of molinate. A 12 ppm solution of molinate (I) in distilled water was photolysed for one half-life (30 min) in the presence of a 100 mg/L suspension of  $\text{TiO}_2$ . Analysis of an extract of this photolysate by mass spectrometry allowed identification of six products (Fig. 4); wet chemical methods provided evidence for the formation of hexamethyleneimine (VIII) and molinate sulfoxide (VI), and HPLC analysis provided evidence of molinate sulfone (VII). 4-Ketomolinate (III) was the major persistent product, reaching a maximum concentration of 3.3 ppm from the 12 ppm molinate solution and then declining (Fig. 5); it also was the major product of  $\text{ZnO}$  oxidation of molinate, and the other products also were nonpersistent.

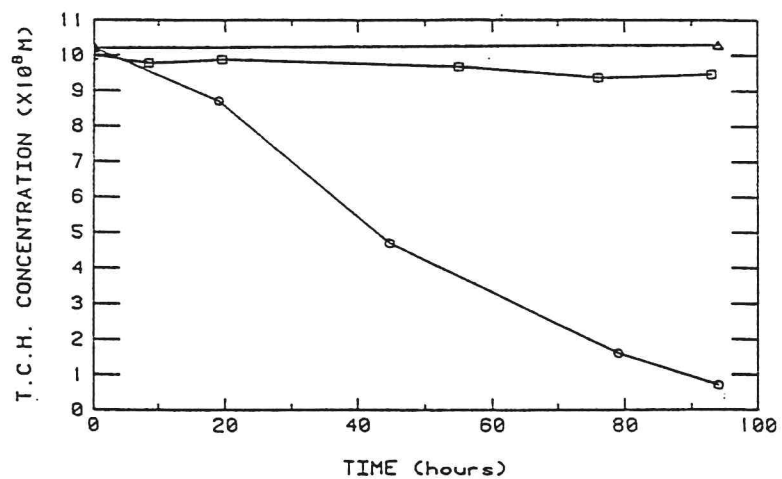


Fig. 1. Degradation of tetrachlorocyclohexanol (TCH) by HO generated from UV light and ozone in the presence of (□) and absence (○) of CO<sub>2</sub>. Δ = Dark control (no CO<sub>2</sub>).

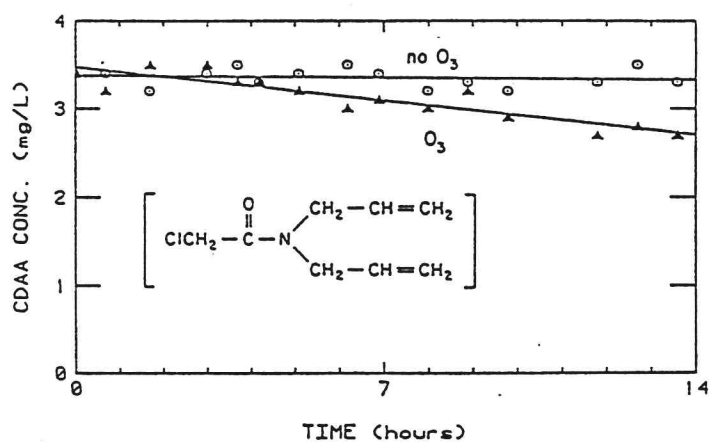


Fig. 2. Reaction rate of O<sub>3</sub> with CDAA (▲) in UV light, compared to UV alone (⊙).

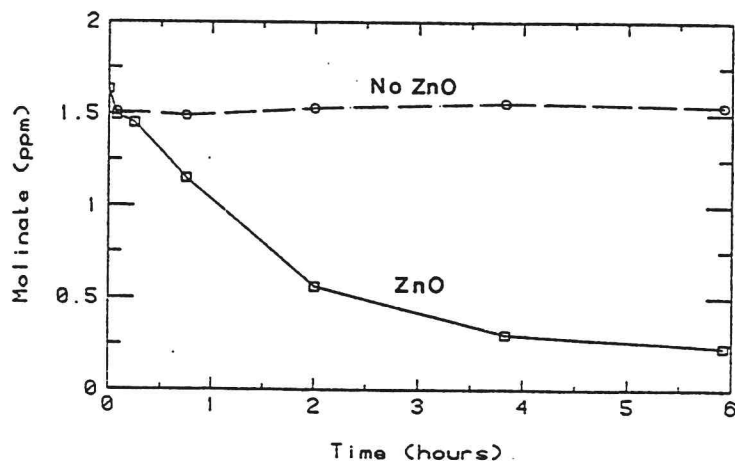


Fig. 3. Degradation of molinate in the presence of ZnO and UV light.

3. Microcosm volatilization modeling. Although the computer-controlled microcosm design reported in 1983 basically did not change, rewriting of the controlling software resulted in improved performance and reliability. As reported last year, this system (containing Ordram 10G) successfully simulated the molinate concentration profile of the 1983 field, despite the unusual conditions (evening application, long half-life of 6.02 days). However, a constant-temperature experiment using that field's average temperature (28°C) gave very different results (Fig. 6A) which were more in accord with "typical" molinate applications. Clearly, the discrepancy was due somehow to varying temperatures.

Not only the difference between varying and constant temperatures but the timing of the varying curve proved important. Microcosm simulations using the same temperature profile, but shifted by 12 hours (simulating an early morning application) gave a molinate profile similar to that from the average-temperature run. Volatilization experiments with technical (unformulated) molinate under the varying and constant temperatures gave identical half-lives (1.6 days), leaving desorption from the granular formulation as the most likely cause of the discrepancies. Comparing this desorption under the varying and constant temperatures (Fig. 6B) showed that in a varying-temperature run, the usual desorption maximum at about 18 hours was suppressed by a simultaneous minimum in temperature, resulting in continued desorption out past 30 hours. This extension of desorption perturbed the volatilization curve in both the field and microcosm, increasing the apparent half-life.

When we mathematically subtracted the desorption curve from the dissipation curve, we obtained results which provided the same half-life (1.6 days) as in the technical molinate volatilization experiments. This demonstrates that the microcosm was able to simulate the unusual molinate application and carry through a series of volatilization and desorption experiments that explained the behavior of the herbicide under those conditions. It also suggests that the herbicide formulation's interaction with varying temperature might be used in shaping concentration profiles for weed control which could improve the performance and persistence of granular formulations such as Ordram 10 G.

4. Analysis of Organic Solutes in Water: A New Method. Most analytical methods for organics in water are intended to measure only a single chemical, and multiresidue "broad spectrum" methods tend to be slow and tedious. For a trace unknown, the recovery often is uncertain, the compound may be unstable under harsh treatment, and the method may not be compatible with instruments used for structure determination.

We have developed a method that minimizes these disadvantages. It provides sensitive analysis for aqueous organics that offers a wide spectrum of selectivity and structure determination from a simple, mild, two-step sample preparation. In step one, the raw water sample (2-50 mL) is flash-frozen in dry-ice and freeze-dried overnight; in step two, the resultant residue is treated with a

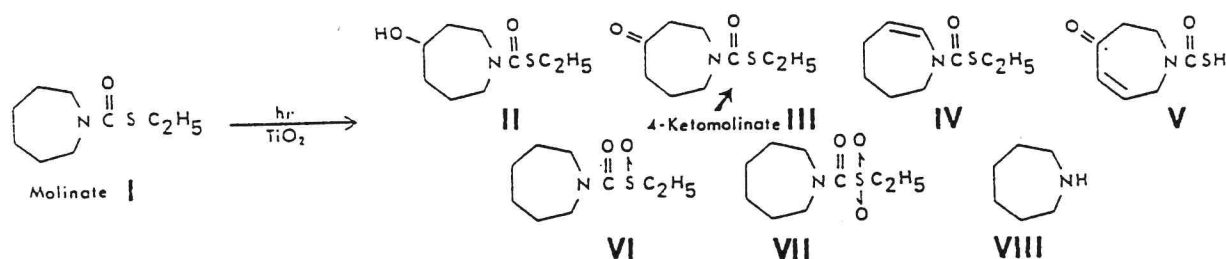


Fig. 4. Photolysis products from molinate in the presence of  $\text{TiO}_2$ .

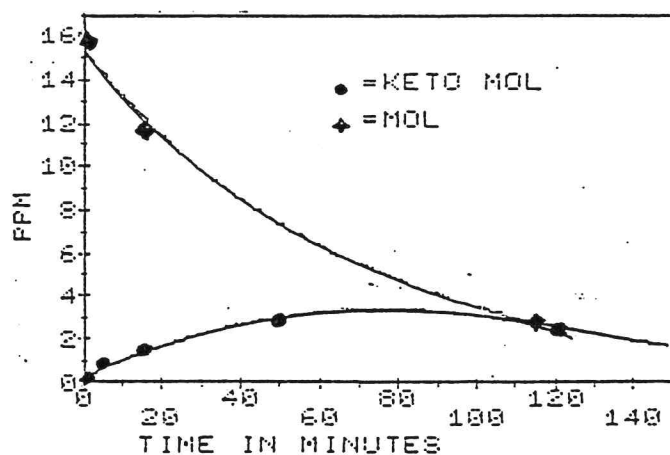


Fig. 5. Formation of 4-ketomolinate (●) in relation to molinate degradation (◆) caused by  $\text{TiO}_2$ .

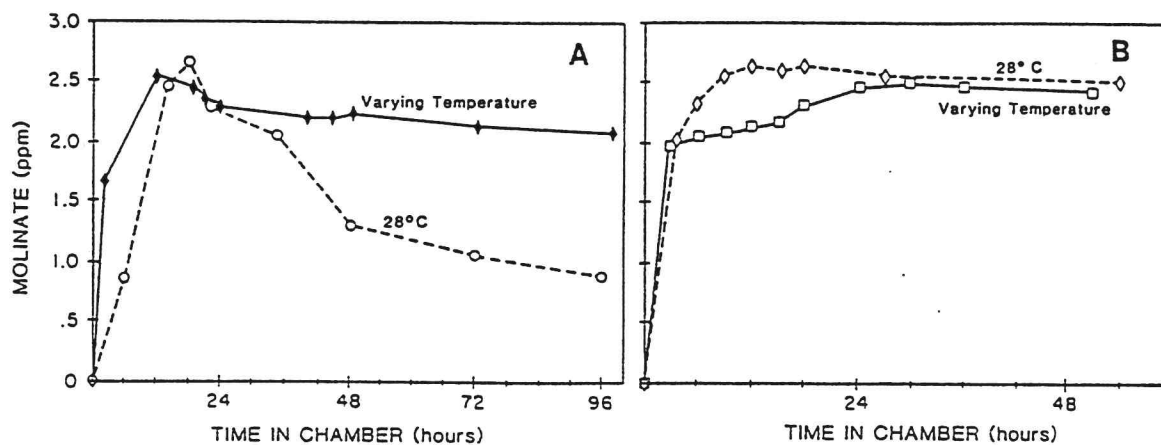


Fig. 6. Molinate dissipation in the microcosm (A) at constant 28° (○) and at temperatures fluctuating as in the field (◆), compared (B) with release rate of molinate from Ordram 10G.

reagent (MTBSTFA), mixed from 1-4 hours, and analyzed by capillary GC or capillary GC-MS.

Central to this method is the ability of the newly-introduced MTBSTFA [N-methyl-N-(tert-butyldimethylsilyl)-trifluoroacetamide] to react with a wide variety of exchangeable hydrogens in high yield, allowing polar and non-volatile substances to be analyzed along with the normally gas-chromatographable compounds. In applying this method for analysis of pesticides and their breakdown products in ricefield water, we have already tested it successfully on organic acids, amino acids, and bentazon. Examples of uses in our research include laboratory and field work on pesticide fate and the screening of rice water for incidental organics that may play a role in the production of natural oxidants.

5. Degradation of Londax by Light. Londax is a new, experimental herbicide from DuPont in which Project RP-1 has indicated continuing interest. It also represents a new chemical class, the sulfonylureas, about which little environmental information exists. We have isolated the active ingredient from Londax formulation, purified it, and developed an analytical method for it based on HPLC. The compound does not absorb UV light in the sunlight region and so was stable in distilled water; however, in dilute hydrogen peroxide solution, at least 8 degradation products were detectable, and their identity is being pursued.

## B. Objective II.

1. Concentrations of Atmospheric Ozone over Rice Fields. The possible direct effects of atmospheric ozone depend upon its atmospheric concentration and availability at the field surface. To determine this, ozone concentrations were measured over several California rice fields with an electronic ozone monitor. Temperatures above 40°C, minimal advection (<1m/s), and a temperature inversion caused ozone levels in nearby Sacramento to reach 0.18 ppm. Ozone was monitored at one m over four rice fields in a line extending from Sacramento towards the northwest; levels reached 0.065 - 0.079 ppmv at each location, consistent with those previously recorded in other rural settings.

As ozone is known to react with soil and plants, we measured the extent to which natural surfaces might deplete the available ozone. Limited atmospheric turbulence allowed determination of vertical ozone profiles up to 2 m above various natural surfaces: over an open drainage canal, 5 m from obvious plant cover, no significant ozone gradient was observed down to 2 cm (Fig. 7A); ozone transport into water was much slower than its atmospheric mixing, and the concentration conventionally measured at 1 m was available at the surface of open water.

Concentrations over a dry dirt road (Fig. 7B) were reduced below 40 cm, and especially below 10 cm, suggesting soil-ozone interaction. Flooded fields with standing rice plants showed a sharp reduction in the ozone level near the water surface (Fig. 7C); ozone



concentrations were reduced even above the 50 cm crop height, and the concentration at 2 cm above the water surface was only 36% of the value at 2 m. Destruction of ozone by rice plants was comparable in each of four fields studied.

We conclude that even under favorable conditions, the surprisingly high atmospheric  $O_3$  levels over rice fields are so reduced by the crop that only a small proportion would impinge upon the water surface, and much of that would react only with surface film. Atmospheric  $O_3$  is not a major degradative force on rice pesticides.

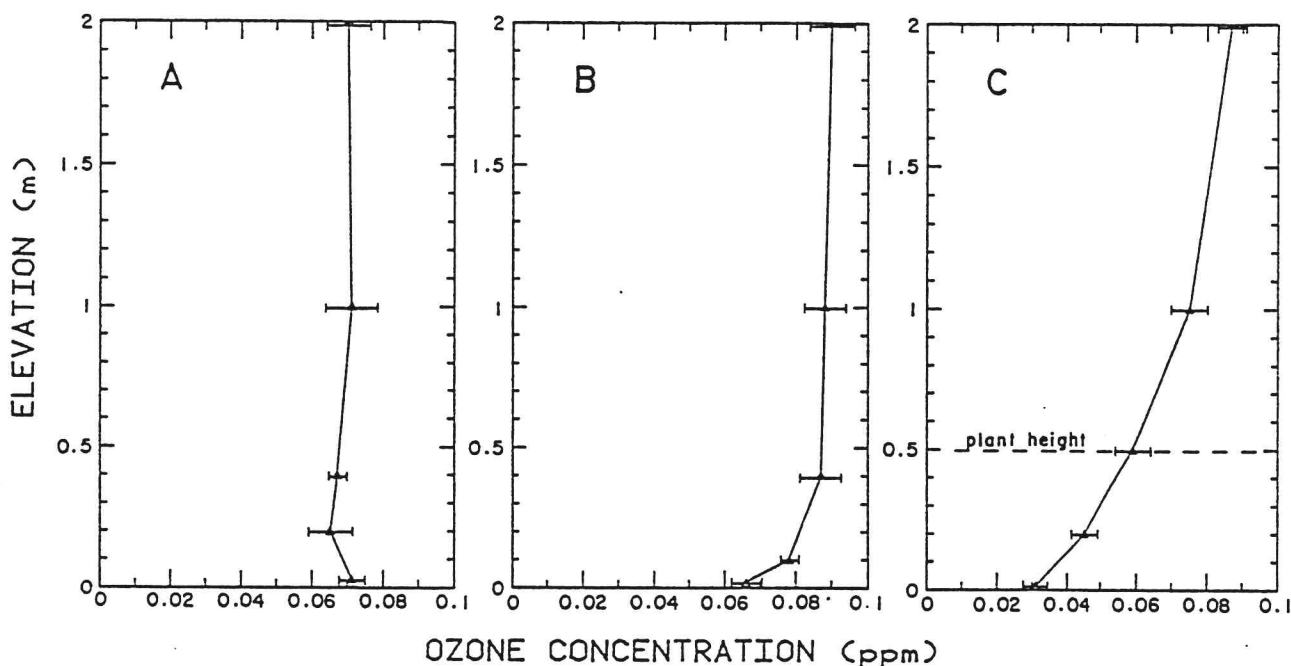


Fig. 7 Vertical ozone profiles over open water (A), dry soil (B), and an established rice stand (C).

2. Sampling and Analysis of Molinate Field Residues. The improved method of molinate analysis described in our 1983 Report has been very successfully applied to the large number of field water samples from the 1984 water management trials (supported primarily by the State Water Resources Control Board). Hundreds of samples were collected, processed, and analyzed with recoveries of 90-110% and 1-10 ppb sensitivity. The 24 plots and 4 inlets received general monitoring for 32 days, and 3 plots also were intensively monitored for 8 days; detailed results will be reported later, but a brief summary is provided in Table I.



Table I. Summary of General Monitoring Results

Water Depth	Holding Time (d)	Treatment #	Average Molinate (ppb)				Aver. Half-life (d)
			Day 2	8	16	32	
High	8	1	1570	450	60	nd	2.9 ± 0.4
	8	3	1200	480	49	nd	2.9 ± 0.5
	8	5	1580	490	80	nd	3.3 ± 0.3
	8	8	1670	500	dry	nd	~ 3.3
	16	6	1470	480	80	nd	3.4 ± 0.4
	32	7	1440	490	110	nd	3.8 ± 0.4
Medium	8	4	2090	500	70	nd	2.8 ± 0.5
Low	8	2	1720	440	60	nd	2.9 ± 0.5

The principal conclusions were (1) that molinate residues from all post-flood applications were remarkably uniform on any given date (about 1400 ppb on Day 2 after application, 500 ppb on Day 8, 60 ppb on Day 16, and undetectable on Day 32), with half-lives all close to 3 days; (2) pre-flood soil incorporation resulted in much lower water residues (80 ppb at 2 days after flooding and 40 ppb after 6 days); (3) half-lives were largely independent of water depth, holding period (over 8 days), or water movement; (4) irrigation water coming into each plot already contained considerable molinate; and (5) residues fluctuated widely, in a cyclical manner, over short time periods--presumably in relation to temperature--so that measured molinate levels were highly dependent upon the exact time of sampling.

Surprisingly, molinate residues in water coincided roughly with temperature--the higher the temperature, the higher the residue--(Fig. 8A) suggesting a possible association with desorption of molinate from sediment. It also is apparent from Fig. 8B (the same residue data) that, depending upon the time chosen for the usual daily sampling, dissipation curves and half-lives could be derived from the scattered points which would differ drastically from each other. This helps to explain differences among State agency data and the variability in our own general monitoring results; apparently, samples always should be taken close to the same time of day--3 pm for maximum residues and 9 a.m. for average figures.

### C. Objective III.

1. Comparative Molinate Analysis. 1983 field water samples analyzed for molinate by the California Department of Agriculture, California

Department of Fish and Game (CDFG), and the Stauffer Chemical Company showed as much as 50% variation among the results. At the request of the State Environmental Hazard Assessment Committee (SEHAC), we conducted a comparison of the CDFG, Stauffer, and UCD analytical methods for molinate in American River water containing known (added) levels between 50 and 500 ppb. In our hands, recoveries were excellent (97-103%), and there were no statistically-significant differences among results at any level. The methods appear equivalent.

In another comparison, we distributed water samples containing known (ppb) levels of both molinate and thiobencarb, similar to those found in the Sacramento River, to 7 commercial and State Analytical laboratories using one or more of the three methods. Again, the results (with one exception) were within 10% of the correct value. We now believe that the original discrepancies may have been due to faulty sampling and that the method of analysis can remain a matter of individual choice. However, where the other methods required a man-week to man-month for 30 samples, the UCD method can produce 30 analyses per day.

2. Enhanced Photo-oxidation Field Experiments. ZnO was selected for limited field trials. Field plots at Biggs and Davis consisted of 8'-diameter aluminum rings set in a larger flooded field, and molinate was applied at 6.3 kg/ha as Ordram 10G. After 3 days, rings were sprayed with ZnO suspended in water (1g/L) at rates equivalent to 12 kg Zn/ha (Biggs), 14 kg/ha, and 6.7 kg/ha (Davis). Plots were intensively monitored for molinate and (at Davis) for 4-ketomolinate, pH, temperature, and dissolved oxygen. Plots were replicated, and control plots received no ZnO.

No significant change in molinate dissipation was observed in the Biggs plots, and subsequent research showed the lack of effect to be due to a surprisingly low pH. However, the Davis experiments were highly successful (Fig. 9): The control half-life of 58 hours was abruptly reduced to 1.5 hours (14 kg Zn/ha) and 2.3 hours (6.7 kg Zn/ha), respectively, by ZnO. The 4-ketomolinate which formed also dissipated, but at a slower rate (Fig. 10).

Zinc normally is added as the sulfate to rice fields as fertilizer at 9-13 kg Zn/ha before flooding, but ZnO also has been used successfully. The ZnO normally is inert but, in water and sunlight, it is solubilized within several days. The present enhanced photooxidation research suggests that aerially-applied ZnO suspension might be applied to flooded rice fields during the holding period both to control herbicide residue levels and serve as the source of micronutrient zinc. However, more extensive field tests are required to assess the nutrient value of such treatments and assure that no damage is caused to the crop.

3. Rice Pesticide Data Bank. Card files containing abstracts dealing with molinate (Ordram) have been accumulated this year. These abstracts represent scientific and technical literature, government documents, reports from agencies, industrial laboratories and

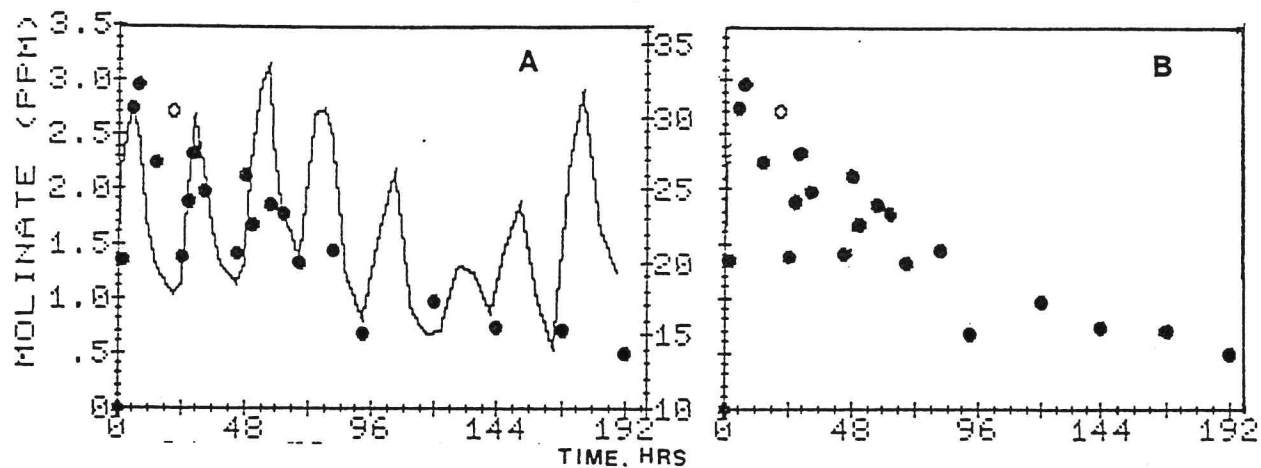


Fig. 8 Relation of molinate field residues to water temperature (5-7" depth of water).

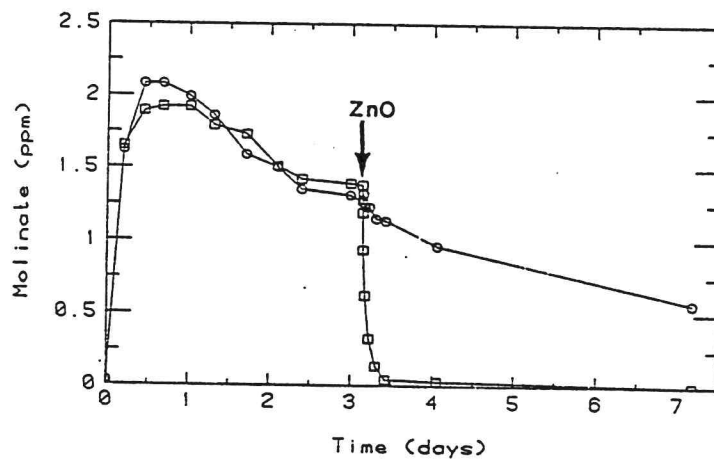


Fig. 9. Field residues of molinate in the presence ( □ ) and absence ( ○ ) of ZnO (12 lbs Zn/acre).

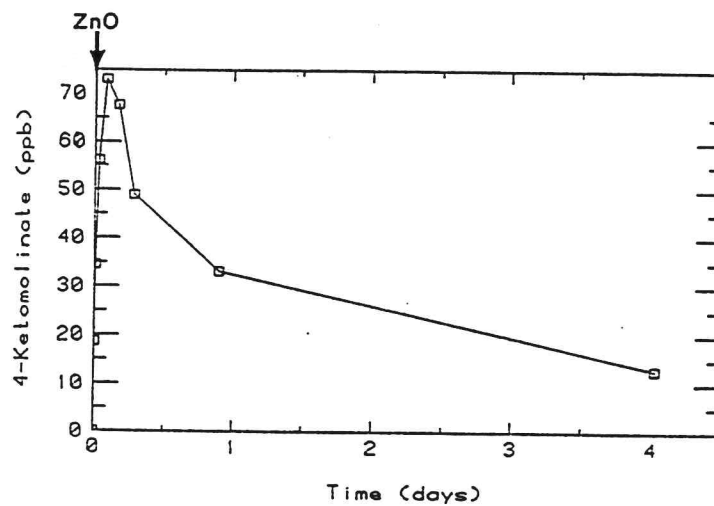


Fig. 10. 4-ketomolinate field residues after ZnO application. None was detectable in ZnO-free plots.

professional societies, and manufacturer's technical data sheets, etc. In addition, various abstracting services and computerized databases have been searched so that our collection will contain all available published information. Articles or reports that are not readily available in the Environmental Toxicology Library are being obtained either through interlibrary loan or direct purchase.

Both the MCPA and the molinate card files are now being classified according to the following broad categories:

- General
  - Chemistry/chemical and physical properties
  - Analysis and determination
  - Environmental fate - air, water, soil, crops, etc.
- Toxicology
  - Toxicity
  - Metabolism/degradation
  - Mechanism of toxic action
  - Effect on target and nontarget organism or species
  - Human exposure (public health and occupational safety)
- Regulatory status

These two files will form the bases for future compilation of monographs or special pamphlets on their known physical, chemical, and biological properties designed primarily for applied researchers, farm advisors, state agencies and interested growers.

Next year, information on thiobencarb (Bolero), a heavily used rice herbicide and a high-priority candidate for the development of a database, will be gathered if its use and production continue. Additionally, efforts will be made to investigate the use of our micro-computer not only to store, retrieve, and disseminate rice herbicide information, but also to provide better access to others not close to the Davis campus.

#### PUBLICATIONS OR REPORTS:

- W.M. Draper and D.G. Crosby. 1984. Solar photooxidation of pesticides in dilute hydrogen peroxide. J. Agr. Food Chem. 32:231-37.
- W.M. Draper and D.G. Crosby. 1984. Photochemistry and volatility of drepamon in water. J. Agr. Food Chem. 32:728-33.
- M.B. Freiberg and D.G. Crosby. 1984. The influence of atmospheric ozone on organic solutes in water. Abstr., 187th National Meeting, American Chemical Society, St. Louis, Missouri, April, 1984.
- R.M. Higashi and D.G. Crosby. 1984. Volatilization modelling of a rice herbicide in a physico-chemical microcosm. Abstr. 188th National Meeting, American Chemical Society, Philadelphia, Pennsylvania, August, 1984.

#### CONCISE GENERAL SUMMARY OF CURRENT YEAR'S RESULTS:

The improved analytical method for molinate (Ordram) and thiobencarb (Bolero) reported last year was tested against standard methods used routinely by the manufacturers, the California Departments of Fish and Game and Food and Agriculture, and others. All of the methods were comparable, but the UCD method was much faster and less expensive than the others.

This improvement was of great importance in this summer's analysis of the large number of water samples generated in a series of Colusa County water management trials. No matter what the trial, molinate residues were about the same on any given day, and the half-lives always were about 3 days, except that pre-flood soil incorporation resulted in much lower water residues after flooding. Half-lives were largely independent of water depth, holding period beyond 8 days, and whether water was still or flowing. Intensive monitoring showed that residue levels varied widely with time of day, so that the usual daily sampling must always be done at the same hour to get consistent and accurate results. The usual waste-management practices may not influence residue levels as much as had been expected.

Similar "unusual" fluctuations of molinate levels have been modelled successfully this year in the laboratory microcosm ("model ricefield") and were found to involve an interaction between release from the granular formulation and temperature. Changes in formulations and time of application might provide control over residues; however, as expected, physical and chemical processes in rice fields turn out to be complicated, and not much seemingly can be done about the physical forces. Chemical breakdown of pesticides might be manipulated by control of oxidation, but the hoped-for importance of atmospheric ozone in this regard proved not to be the case--ozone has little effect on rice pesticides in the field.

Intentional addition of oxidants also might work, as presented in last year's report. Laboratory experiments now show that solid zinc oxide--once experimented with as a source of micronutrient zinc--can generate pesticide-degrading oxidant in sunlight quite efficiently. In a limited field test, spraying a dilute aqueous suspension of zinc oxide 3 days following Ordram 10G application caused abrupt loss of molinate residues in the water over the course of only a few hours. The identified breakdown products were harmless and nonpersistent.

While a lot remains to be done to assure the safety and adequacy of zinc oxide as a means of controlling pesticide residues in rice fields, this new approach at least offers the possibility that residue control could be as simple as adjustment of the time at which zinc fertilizer is used.