

COMPREHENSIVE RESEARCH ON RICE
ANNUAL REPORT

January 1, 1983 - December 31, 1983

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

PROJECT LEADER AND PRINCIPLE UC INVESTIGATORS:

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LEVEL OF 1983 FUNDING: \$26,200.

OBJECTIVES AND EXPERIMENTS CONDUCTED BY LOCATION TO ACCOMPLISH OBJECTIVES:

- A. Objective I. To identify, investigate, and model environmental factors which govern movement and chemical fate of rice pesticides.
 - 1. Development and calibration of an environmental ozonolysis chamber (UC-Davis).
 - 2. Improvement of the ricefield microcosm (UC-Davis).
 - 3. Improvement of analytical methods for molinate (Ordram) and thiobencarb (Bolero) (UC-Davis).
 - 4. Modelling of molinate and Ordram volatilization under standardized conditions (UC-Davis).
 - 5. Synthesis, purification, and reactions of thiolcarbamate sulfoxides (UC-Davis).
 - 6. Development of procedures for investigation of rice-herbicide metabolism in fish (SWRCB) (UC-Davis). See C.4.
- B. Objective II. To estimate the relative importance of such factors to the practical use of specific rice pesticides.
 - 1. Sampling and residue analysis of rice fields treated with Ordram, Bolero, and MCPA (Glenn County, CA.).

2. Comparison of molinate field-dissipation with that predicted by the microcosm (UC-Davis).
 3. Comparison of dissipation of fenitrothion- and parathion degradation products (UC-Davis).
- C. Objective III. To apply research results toward meeting regulatory requirements and improved management of rice pesticides.
1. "Catalysis" (enhancement of herbicide photo-oxidation (UC-Davis)).
 2. Collaboration with the Sacramento Water Department (UC-Davis).
 3. Analysis of well-water at the Rice Experiment Station (Biggs, UC-Davis).
 4. Parathion metabolism and residues in rice-field crayfish (UC-Davis).
 5. Rice pesticide data bank (UC-Davis).

SUMMARY OF 1983 RESEARCH (MAJOR ACCOMPLISHMENTS) BY OBJECTIVE:

A. Objective I.

1. Effect of Atmospheric Ozone on Rice Herbicides. Ozone is a strong oxidant present in the lower atmosphere at concentrations up to 0.1 ppm and reported at this level over rural farm land. It also is known to react with water to produce hydroxyl radicals, shown in our previous reports to have an important place in the degradation of rice herbicides. The purpose of our present experiments is to determine the possible significance of ozone in the dissipation of rice pesticides.

The procedure used previously (1981 Report) to examine the effect of ozone-containing air on MCPA has a number of drawbacks for other chemicals, especially increased volatilization. An environmental chamber was developed (Fig. 1) in which pesticide solutions in water could be irradiated with sunlight-ultraviolet (UV) under a constant surface-exposure to known levels of ozone in air. An analytical method was devised, using ozonolysis of an intensely-colored indigotrisulfonate dye, which showed that the air-water ozone flux was close to that reported for the outdoor environment (0.3 moles/acre/day).

To test the system, the ozonolysis rates of several model compounds were measured. The reaction of ozone with 2,4-dichlorophenol (a 2,4-D breakdown product) was moderately rapid in the dark but was obscured by purely photochemical degradation in light (Fig. 2); nitrobenzene did not react with ozone in the dark but again was photolyzed in UV light, while p-nitrophenol (a parathion degradation product) was not appreciably photolyzed but was degraded by ozone in both dark and light.

Preliminary tests showed that both MCPA and thiobencarb were stable to ozone in the dark while degraded in light, but the relationship between effects of light, ozone, and hydroxyl radicals still is unclear without further experiments (in progress).

2. The Ricefield Microcosm. The prototype microcosm ("model ricefield") described in our 1982 Report has been greatly improved. In particular, a simple but very successful electronic heating and cooling system (based on a thermoelectric chip) has been designed and built by Mr. Higashi; this now is controlled by a microprocessor (computer) which is programmed to afford preset diurnal temperature changes closely simulating those of a ricefield. Incorporation of computer-controlled variation in pH is in progress. Material for a UV-transmitting lid has been obtained, and several hundred pounds of rice-field mud has been dried, sieved, and blended in preparation for future experiments.

3. Improved Molinate and Thiobencarb Analysis. The analytical detection and measurement of molinate and thiobencarb in water has been greatly improved. Instead of solvent extraction, the sample is poured through a short column of exclusion resin, the pesticide washed through with solvent, and the resulting solution analyzed directly by gas chromatography (GLC). At least 80 analyses can be conducted per day with >98% recovery efficiency and 1 ppb sensitivity. This method has been employed in many of our other experiments during the year.

4. Volatilization Modelling. Additional microcosm experiments were conducted to achieve an operation which would approximate our standard field dissipation for molinate (residue maximum at 18 hrs, $t_{1/2} = 58$ hrs at 28°C) as closely as possible. By redesigning a tighter lid, improving temperature control, and minimizing vapor losses during analytical sampling, the microcosm provided a satisfactory maximum-residue time and smooth first-order dissipation (Fig. 3), but the dissipation rate ($t_{1/2} = 38$ hrs) was too great. Reducing the average temperature to 25°C produced anomalous results. The problem will be seen again in Part B.2 of this report; efforts to solve it are in progress.

5. Thiolcarbamate Sulfoxides. The sulfoxides of molinate and thiobencarb are important degradation products — "Bolero sulfoxide" is suspected of contributing to off-flavor in Sacramento City Water — but analysis has been unsatisfactory. In order to investigate their environmental and analytical properties, improved methods were developed for their laboratory synthesis and purification. Hypochlorite oxidation of the herbicides followed by silica-gel chromatography, with fractions monitored by thin-layer chromatography (TLC), allowed collection of gram-quantities of sulfoxides and sulfones with high efficiency.

The chemical properties of thiolcarbamate sulfoxides have remained largely unknown. Many experiments were conducted on the oxidation, reduction, and other reactions of thiobencarb sulfoxide with the particular purpose of finding a better means of analysis; a few are summarized in Table I. Products were separated and identified by GLC, TLC, and other methods. Where reactions occurred, however, a mixture of products always was obtained in which no single constituent was present

Table I. Some reactions of thiobencarb sulfoxide.

Solvent	Reagent	Product(s)
Ethanol	HCl	T, CBA
Ethanol	HCl/NaCl	T
Ethanol	Diethylamine	T, CBA
Ethanol	NaBH ₄	T
DMF	NaOH	TSO ₂
Ethanol	NH ₄ OH	T, BCE

T = thiobencarb, TSO₂ = sulfone, CBA = p-chlorobenzoic acid,
BCE = 1,2-bis(p-chlorophenyl)ethane

in large enough proportion to afford a new analytical method. At present, the best method for analysis of thiobencarb sulfoxide in water is by HPLC with a UV-absorption detector (C₁₈ reverse-phase column, 1:5 water-methanol solvent, 10 ng = 1 ppm sensitivity).

B. Objective II.

1. Field Sampling and Residues. Water sampling was conducted in June, 1983, in three separate fields in Glenn County in coordination with California Department of Food and Agriculture (CDFA) tests. The fields received commercial applications of Ordram 10G, Bolero 10G, and MCPA (DMA salt); temperature, pH, dissolved O₂, and UV intensity were measured by us, and CDFA additionally measured air temperature, wind velocity, and relative humidity.

The samples from Ordram and Bolero treatments were analyzed by the simplified method described above; MCPA samples still are being held in cold storage. The dissipation curves are shown in Figs. 5 and 6. The molinate half-life ($t_{1/2}$) was 6.02 days (144 hrs), with the maximum concentration at 0.5 day (12 hrs), and that of thiobencarb was 7.22 days (173 hrs) with the maximum concentration at 2.25 days (54 hrs). The weather at application time was cool and unsettled, with some rain during the test period, and the Ordram-treated field was drained prematurely — none of them "normal" conditions. It is apparent from Figs. 5 and 6 that the dissipation did not provide the usual symmetrical curves (see Fig. 3) and the dissipation of both was much slower than that seen in previous years (molinate $t_{1/2}$ = 2.4 days and thiobencarb $t_{1/2}$ = 4.5 days, normally).

Two observations were of particular interest and importance, both to residue monitoring and modelling. First, in the molinate field trial, at least, the water entering the field was found already to contain over 1 ppm of the herbicide. As a 3 kg/ha (3 lb/acre) application would be expected to result in only 2 ppm in water 6 inches deep,

this represents a significant addition of herbicide. Second, in distilled water in containers sunk in the field and carefully guarded from contamination, reabsorption of molinate vapor from the atmosphere amounted to another 0.12 ppm, suggesting continual molinate exposure even in untreated fields.

2. Microcosm Prediction of Field Data. Ordram 10G and Bolero 10G were applied separately to a 15 cm depth of water in the microcosm at rates corresponding to those used previously in the field. The water temperatures were regulated by computer to correspond to those actually measured during the field test, including the peculiarities; samples were collected and analyzed, and the microcosm dissipation was compared to the field dissipation. A comparison also was made with microcosm data obtained at the constant average temperature of the field (28°C).

Fig. 7 shows the excellent correspondence of lab and field data for Ordram; smoothing the curves to fit a predicted first-order dissipation (Fig. 8) also shows the close correspondence. However, correspondence of the curve generated at constant rather than continuously-variable temperature was very poor (Fig. 9). This discrepancy remains unexplained at present.

3. Dissipation of Fenitrothion- and Parathion Breakdown Products. Parathion and methylparathion applications to California rice exceeded 117,000 pounds of actual ingredient in 1982. Lab data indicate that photooxidation and subsequent hydrolysis are slow ($t_{1/2} = 200$ days) (although field data for California conditions are not readily available); the principal breakdown product is p-nitrophenol (PNP), whose degradation (by hydroxyl radicals) and volatilization are negligible.

A closely related organophosphorus insecticide called fenitrothion (Sumithion, O,O-diethyl (3-methyl-4-nitrophenyl)phosphorothiolate) is not presently registered on rice in the US but is very important in Asia. It is rapidly photooxidized and hydrolyzed to give the corresponding 3-methyl-4-nitrophenol and other products. Our 1983 lab tests indicated that this phenol was stable in the dark in aqueous solution but rapidly degraded by photolysis to a large number of nonpersistent products. Standards of the most obvious possibilities were synthesized, and high-pressure liquid chromatographic analysis and TLC indicated that oxidation of the ring-methyl group is a key process in the destabilization. As the breakdown of the "nonpersistent" parathion and methylparathion has the potential for releasing over 50,000 pounds of toxic PNP into the environment each year, the fenitrothion data suggest that this substitute might be worth investigating for ricefield uses to avoid future residue problems.

C. Objective III

1. Enhanced Herbicide Photooxidation. The initial and principal degradation of all the rice pesticides we have investigated is by oxidation, generally by sunlight-energized reagents or reactions. A number of simple reagents (such as hydrogen peroxide) are capable of carrying out these oxidations, and others (such as dyes) should enhance

or "catalyze" them. Several metal oxides (including the white paint pigment, titanium dioxide) long have been known to generate hydrogen peroxide from atmospheric oxygen under UV light.

A lab system was devised which allowed samples to be taken from sealed glass vessels while the contained dilute aqueous solutions of molinate or thiobencarb were irradiated with sunlight UV. Analysis by our improved method allowed degradation half-lives ($t_{1/2}$) to be established to determine the relative effectiveness of added oxidants. Ten chemical oxidants were tried initially, and the results are summarized in Table II; a typical degradation curve is shown in Fig. 4 for the most intriguing of the enhancers -- simply a suspension of insoluble titanium dioxide (0.1 mg/mL) -- which oxidizes molinate and thiobencarb with a $t_{1/2}$ of about 30 minutes.

The results raise the possibility that the herbicides might be at least partially degraded intentionally as they move out of treated rice fields when water is released. While some of the reagents appear impractical (for example, zinc oxide might add undesirable levels of zinc to the water), persulfate, hypochlorite, and titanium oxide hold promise. Products have not yet been identified.

2. Collaboration with the Sacramento Water Department.

Collaboration with chemists at the Division of Water and Sewers has continued on analysis of herbicides and degradation products --

Table II. Enhanced Oxidation of Thiolcarbamate Herbicides^a

Additive	Molinate $t_{1/2}$ (min)	Thiobencarb $t_{1/2}$ (min)
Zinc oxide	30	6
Titanium dioxide	30	40
Sodium hypochlorite	very fast	-- ^b
Potassium persulfate	20	15
Hydrogen peroxide	170	--
Oxygen	NR ^c	NR
Acetone	NR	NR
Sodium nitrite	NR	NR
Potassium nitrite	NR	--
Ammonium nitrate	NR	--

^a Initial herbicide concentration 12 ppm, oxidant molar ratio 1000:1.

^b Not tested.

^c No appreciable reaction.

especially thiobencarb sulfoxide — in drinking water. While thiobencarb and molinate exist for a few weeks at the Sacramento River Water inlet, no herbicides or degradation products have been detected in treated water.

3. Analysis of Rice Research Station Well-Water. There presently is widespread concern that pesticides — especially the volatile ones such as molinate -- will move into ground-water. Our extensive 1982 tests for MCPA in well-water from Sacramento Valley locations revealed no detectable traces (<0.5 ppb). At the request of Dr. Morton Morris, Director of the Rice Experiment Station at Biggs, well-water from the Station was tested frequently during and after 1983 pesticide applications in the area. At 1-month intervals, from May through October, 1983, Station well-water was passed through columns of exclusion resin and the tubes held frozen for later elution, fractionation, and analysis by GLC or HPLC.

2,4-D, MCPA, DDT, DDE, dieldrin, and parathion were not detected at a sensitivity level of 0.05 parts per trillion (ppt = 10^{-9} g/L). Similarly, neither molinate (at 2 ppt), thiobencarb (3 ppt), methyl parathion (0.5 ppt), nor carbofuran (50 ppt) was detected, nor was thiobencarb sulfoxide present above 1000 ppt (1 ppb). Traces of other (unidentified) chemicals were present at ppt levels and probably were derived from plumbing fixtures, pump oil, soil organic-matter, etc.

Although this examination required a major effort, it was deemed worthwhile. Logic says that if these common rice pesticides were going to appear in groundwater, the greatest concentrations should occur in the relatively shallow wells located directly in rice-growing areas which receive treatment year after year. As the detectability limits in this work are satisfactorily low, we must assume that residues penetrating to the water table are negligible. Furthermore, the Rice Experiment Station personnel can be assured about the safety of their drinking water.

4. Metabolism and Residues of Rice Pesticides in Aquatic Animals. With funds from the State Water Resources Control Board, grad student Ron Tjeerdema has devised a laboratory system for measurement of the bioconcentration and metabolic detoxication of rice herbicides in common Sacramento River fish, starting with molinate in striped bass. Our similar work (by Greg Foster) with the ricefield crayfish, Procambarus clarkii, has been supported by the National Institute of Environmental Health Sciences and has concentrated on p-nitrophenol (PNP) and the parathions. The recreational harvesting of both species has given rise to concern of possible toxic residues in the animals' flesh. P. clarkii absorbed PNP from water containing 0.1 ppm in 7 hrs to give residues of 4 ppb in tail muscle, 14 ppb in gill, and 35 ppb in the digestive gland.

5. Rice Pesticide Data Bank. Progress has been rather slow this year. The MCPA card file and data collection are essentially complete, and work has started on the molinate file and collection. Carry-over of remaining funds is requested.

PUBLICATIONS OR REPORTS:

- W.M. Draper and D.G. Crosby, The photochemical generation of hydrogen peroxide in natural waters, Arch. Environ. Contam. Toxicol. 12, 121 (1983).
- D.G. Crosby, The fate of herbicides in California rice culture, in "Pesticide Chemistry: Human Welfare and the Environment" (J. Miyamoto and P.C. Kearney, eds.), Pergamon, Oxford, 1983, Vol. 2, p. 339-46.
- D.G. Crosby, "Atmospheric reactions of pesticides," in Pesticide Chemistry: Human Welfare and the Environment" (J. Miyamoto and P.C. Kearney, eds.), Pergamon, Oxford, 1983, Vol. 3, p. 327-32.
- D.G. Crosby, The significance of microenvironment in pesticide photodecomposition, Abstr. 185th National Meeting, Amer. Chem. Soc., Seattle, March, 1983.
- M. Freiberg and D.G. Crosby, The photolysis of MCPA in simulated spray droplets, Abstr. 185th National Meeting, Amer. Chem. Soc., Seattle, March, 1983.

CONCISE GENERAL SUMMARY OF CURRENT YEAR'S RESULTS:

The improved "model rice field" microcosm, with more temperature flexibility and under computer control, has been used successfully to predict molinate volatilization from an actual field application of Ordram 10G. The weather during the 1983 field trial was very abnormal, and molinate dissipation differed significantly from that measured (and modelled) in 1982; the 1983 half-life was 6 days instead of 2 days. However, the microcosm was able to predict the unsymmetrical field-dissipation curve with reasonable accuracy, based on volatility alone. Field variables included residues in inflow water and residue reabsorption from the atmosphere. Analysis of the extensive field and laboratory samples was greatly aided by major improvements in the efficiency of the molinate (and thiobencarb) method. 1983 Bolero and MCPA field applications also were monitored and will be modelled in the microcosm.

Equipment and procedures for investigation of the reaction of atmospheric ozone with rice pesticides were developed. Analysis by dye-decolorization showed that the ozone movement into water in the reactor was close to that found in the field. Initial evidence implicates ozone as a generator of natural field oxidants in water which may exert a profound influence on pesticide persistence. Photooxidation of molinate and thiobencarb by 10 other reagents indicated that herbicide degradation might be intentionally accelerated. Sodium hypochlorite, potassium persulfate, and titanium oxide (white paint pigment) provide the possibility of practical water treatment to lower residues in fields or drains at will.

The principal photodegradation product of parathion and methylparathion -- p-nitrophenol -- was found to be persistent in water. However, the corresponding phenol from a closely-related insecticide called fenitrothion was rapidly photooxidized, suggesting that it should be examined as a possible replacement for the parathions. Parathion was rapidly degraded by ricefield crayfish to p-nitrophenol, which itself was excreted to leave only very small parathion residues in the edible meat. These are the initial steps necessary to understanding residue dynamics in this increasingly-harvested animal.

An extensive but unsuccessful search was made for a new chemical basis to the detection and measurement of molinate- and thiobencarb sulfoxides, but the preparation and purification of sulfoxide standards were improved. The best current analytical method for sulfoxides involves HPLC with detection by UV absorption. Well-water from the Rice Research Station at Biggs was analyzed from May through October for these and the other principal rice pesticides and degradation products, but none was detectable at the part-per-trillion level; apparently, they do not penetrate appreciably into ground-water.

A comprehensive information file on MCPA is essentially complete, and compilation of the file on molinate is underway to provide rapid access to technical information needed by researchers, farm advisors, and growers.

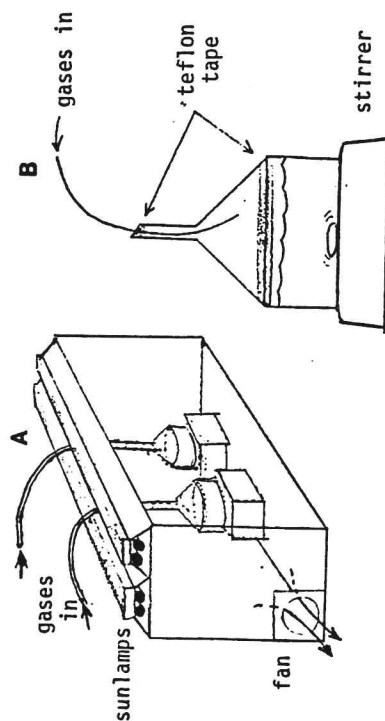


Fig. 1. UV light chamber (A) and an ozone reaction chamber (B).

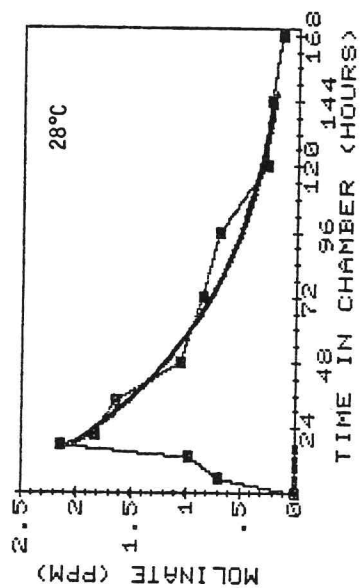


Fig. 3. Ordram 10G volatilization in the microcosm (■), compared to a calculated first-order rate

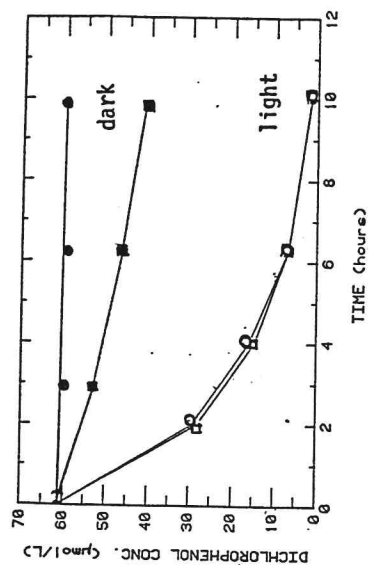


Fig. 2. Loss of 2,4-dichlorophenol in the presence (□) and absence (○) of ozone, in UV light and dark.

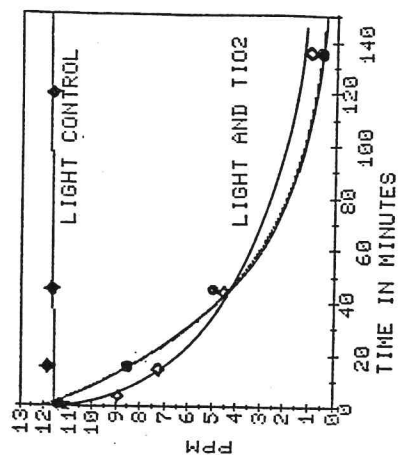


Fig. 4. Photooxidation of molinate (●) and thiobencarb (◻) in the presence and absence of titanium dioxide (TiO_2).

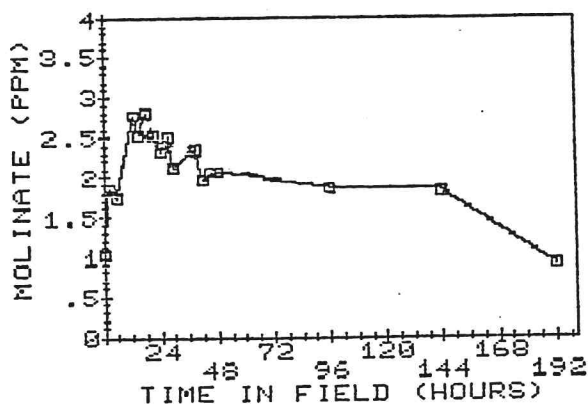


Fig. 5. Field dissipation of molinate from Ordram 10G.

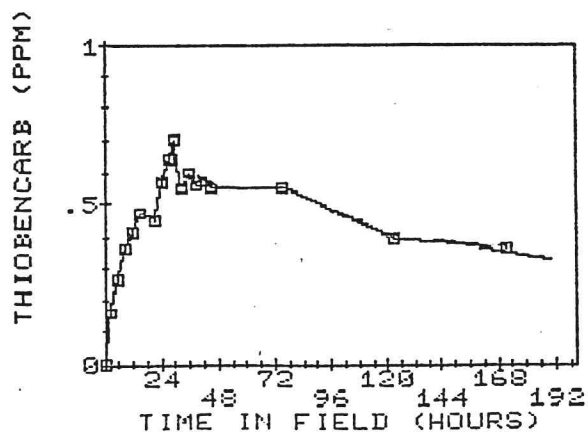


Fig. 6. Field dissipation of thiobencarb from Bolero 10G.

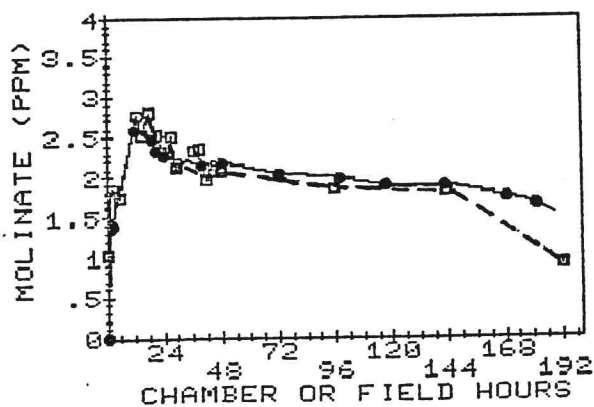


Fig. 7. Field dissipation of molinate (□) from Ordram 10G compared to microcosm prediction (●).

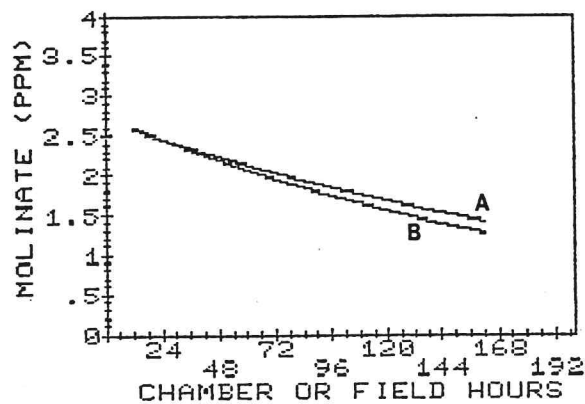


Fig. 8. Calculated dissipation rates for molinate in the microcosm (A) and field (B).

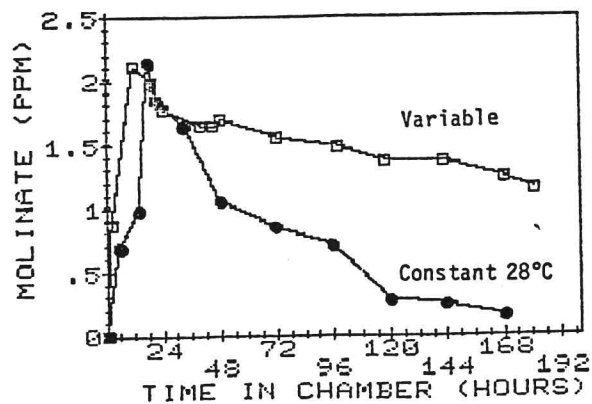


Fig. 9. Comparison of molinate dissipation in the microcosm under constant and variable temperature.