

SUNLIGHT PROTECTION FOR ULV MALATHION?

W. C. Hoffmann and I. W. Kirk
USDA-ARS-APMRU
College Station, TX

Abstract

Ultra-low-volume malathion is the most commonly used insecticide for the control of boll weevils in the United States. With millions of acres being treated each year, any efforts that extend the efficacy and thereby, reduces the amount of insecticide used can translate into significant cost savings to cotton producers. Various chemicals have been reported to extend the time that some viruses used for insect control are efficacious by functioning as ultraviolet protectants. Therefore, a study was conducted to evaluate three of these chemical protectants for their ability to decrease the rate of degradation of ULV malathion.

The chemicals that were tested as protectants were p-aminobenzoic acid (PABA), Congo Red, and Fluorescent Brightener 28. Each of the three protectants was added individually to ULV malathion, applied to cotton plants, and evaluated using leaf bioassays and chemical residue analyses. Each of the three compounds numerically increased the percent mortality in a leaf bioassay test at 0, 3, 6, and 10 days after treatment (DAT) compared to the ULV malathion only treatment. Boll weevil mortality in the protectant chemical treatments was significantly greater than the ULV malathion only treatment at 10 DAT. The treatment that contained Congo Red provided significantly greater mortality than the malathion only treatment at 3 DAT. All of the treatments that contained malathion were significantly higher from the untreated check on all sampling dates. Residue analyses were performed to determine malathion degradation rates. The Congo Red treatment only degraded by 10.8% by 6 DAT. All treatments degraded 59-75% at 10 DAT. The use of Congo Red in a field application of ULV malathion warrants further investigation.

Introduction

Ultra-low-volume (ULV) malathion is the most commonly used control strategy for boll weevils in Boll Weevil Eradication Programs (Jones et al. 1996b). The length of time that this product remains efficacious in the field has a significant impact on the overall control achieved. The time between application and less than 50% efficacy has been reported to be 24 hr (Mulrooney et al. 1997), over 3 days (Villavaso et al. 1996, England et al., 1997), and 6 days (Jones et al. 1996a). Mulrooney et al. (1997) and Hoffmann

(1999) showed that less than 50% of the applied material was present in the field 24-hr after application. Any increase in the longevity of the material could translate into a cost saving for the Eradication Program since it would increase the time between sprays and subsequently, reduce the number of sprays.

Hoffmann (1999) reported that sunlight contributed significantly to the degradation of malathion and suggested that certain materials which prevent sunlight from breaking down the product might increase the longevity of malathion in the field. Optical brightening materials have been used as radiation protectants for various viruses used to control insect pests (Ignoffo and Batzer, 1971, Shapiro, 1989, Shapiro, 1992, and Shapiro and Argauer, 1995). Jaques (1968) suggested that optical brighteners provide protection from degradation by absorbing the ultraviolet (UV) spectrum of sunlight. Tests were conducted to determine if the optical brighteners and dyes reported to protect insect viruses could be used to protect ULV malathion from degradation. The objective of this study was to evaluate optical brighteners and dyes as a means of decreasing the rate of degradation of ULV malathion.

Materials and Methods

Three materials, which have been reported to protect insect viruses from degradation, were chosen to test their ability to increase the longevity of ULV malathion or function as protectants. These materials were: P-aminobenzoic acid (PABA): (Product No. A0129, Sigma Chemicals, St. Louis, MO); Congo Red: (Product No. C6767, Sigma Chemicals); and Fluorescent Brightener 28: (Product No. F3543, Sigma Chemicals).

The PABA and Congo Red at the rate of 1% by weight and the Fluorescent Brightener at the rate of 0.1% by weight were added to ULV malathion (Clean Crop, Platt Chemical Co., Fremont, NB, EPA Reg. No. 34704-565), which contains 95% malathion. Each of the materials was suspended in 20 ml of acetone prior to being added to the ULV malathion to aid in mixing. The malathion and protectant mixtures were compared to ULV malathion only, which also had 20 ml of acetone added, and an untreated check for a total of five treatments. It was assumed that the acetone would evaporate before any of the tests were conducted and would not alter the toxicity of ULV malathion.

Leaf Bioassay

Each treatment was applied to 24 potted plants using a modified spray gun. The modifications were designed to simulate the droplet spectrum produced during an aerial application of ULV malathion. The target rate for these applications was 16 oz of malathion/acre. After the plants were treated, they were held outside for 0, 1, 3, 6, and 10

days after treatment (DAT). Twelve leaves were selected at random from the top of the plants at each DAT. Six leaves were used in a bioassay test and six leaves were used for residue analysis. The bioassay test consisted of placing the selected leaves in individual petri dishes in the laboratory, then placing 10 boll weevils (GAST Rearing Facility, Mississippi State, MS) in the petri dishes. The petri dishes were modified by cutting a hole in the top of the dishes then gluing screen over the hole. This allowed the dish to be ventilated. Tests have shown that mortality can occur in unventilated dishes even if the boll weevil is prevented from coming into contact with the toxicant (Hoffmann, unpublished data).

Residue Analysis

For the residue analysis, six leaves from the top of plants were placed in individual resealable, plastic bags. Samples were placed in an ice chest and transported to the laboratory. After placing 20 ml of ethanol in the bags, the bag was shaken vigorously, with care being taken to adequately wash both sides of the leaf. A 2 ml sample of the rinsate was poured into a glass, sealable vial for gas chromatography (GC) analysis. The leaf was then taken out of the bag and measured using a leaf area meter (Model #LI-3100, Li-COR, Inc., Lincoln, NE). The area measurements were used to convert the deposition data to dosage per unit area. There were no appreciable differences in leaf size across the DAT readings. Malathion was quantified using a Hewlett-Packard 6890 gas chromatograph with flame ionization and a J&W DB-1 dimethylpolysiloxane column (30 m X 0.32 mm X 0.25 μm) with a 2 ml/min flow of helium. The chromatograph and auto sampler were operated with Hewlett-Packard's Chemstation software. The operating parameters for the chemical analysis were: injector temperature - 120°C, detector temperature - 250°C, oven program - 60°C initial temperature held for 2 min, then the temperature was ramped 30°C/min to 220°C, a 5°C/min increase to 230°C, a 35°C/min to 300°C, then held for 2 min. The retention time of the malathion was 9.08 min. The oven was allowed to cool before the next sample was injected.

The data were analyzed as a completely randomized design. All statistical significance refers to the $\alpha=0.05$ level. All means were separated using Duncan's multiple range test.

Results and Discussion

Leaf Bioassay

Leaf bioassays (Table 1) showed that there were no significant differences in boll weevil mortality between the standard ULV malathion treatments and the three protectants treatments for 0 and 1 DAT. The Congo Red treatment had significantly higher mortality than the standard ULV malathion treatment at 3 DAT but it was not significantly different from the other two protectant treatments.

Significant differences were not detected in treatments containing malathion at 6 DAT. The three treatments containing protectants had significantly higher mortality than the standard ULV malathion treatment at 10 DAT. The three protectant treatments had higher numerical efficacy than the malathion only treatment on all but a single DAT. All treatments containing malathion were significantly better than the untreated check on all sampling dates.

The high mortality (>80%) for the three protectant treatments even out to 10 DAT was unexpected. Previous studies have shown that efficacy normally drops to below 50% by 1-3 DAT. The high levels of efficacy may have been a result of the time of the year that the test was conducted. The results that are reported are from the third attempt to conduct this study. The first two attempts were confounded by very high mortality rates (>50% in some dishes) in the untreated checks. There was no known cause of this mortality. Therefore, the test results reported were from a study that started on 7 September. The strength of the sunlight is less than during the normal cotton-growing season when most studies are conducted and may have contributed to less rapid degradation of the malathion. The normal solar radiation strength in June and July in Austin, TX is 6.69 kW-hr/m² but drops to 5.24 kW-hr/m² in September (National Renewable Energy Laboratory website, Golden, CO). There was also no detectable dew during this test. Lower temperatures in September may have also led to the increased longevity of the malathion.

Residue Analyses

Preliminary gas chromatograph screening of the protectants selected revealed that they passed through the column approximately 4 min before the malathion so there was no interference caused by the protectants. No malathion was detected on any of the untreated, check plants. The residue analyses (Table 2), which measured the amount of malathion on the leaves, was expressed as the percent of degradation detected at each DAT compared to that detected immediately after the applications.

The initial or 0 DAT deposits for the PABA, Congo Red, Brightener 28, and malathion only treatments were 18.1, 20.6, 17.9, and 19.1 $\mu\text{g}/\text{cm}^2$, respectively. These deposits were slightly higher than the target rate of 16 oz of malathion/acre or 12.7 g/cm². The PABA treatment had the most rapid degradation of the four treatments. The Congo Red and ULV malathion only treatments had the lowest degradation rates at 3 DAT. The Congo Red had the least amount degradation at 6 DAT. All treatments had degraded by 59-75% by 10 DAT. Congo Red treatment appears to be the most promising UV protectant tested since it degraded the slowest; therefore, additional field studies will be conducted in the following season.

The higher initial deposition rates may have confounded some of the test results. At 6 DAT, the Congo Red treatment had only degraded by 10.8% while the malathion only treatment had a 75% degradation; however, there were no significant differences in mortality. This would lead one to conclude that there was enough malathion left on the plant after the degradation to be efficacious. The nonsignificance at 6 DAT in the leaf bioassay may have also been a result of the high mortality in the checks (13%). There was no known cause for this high mortality in the check.

References

England, M., R. Minzenmayer, and C. Sansone. 1997. Impact of selected insecticides on boll weevil and natural enemies, pp. 989-993. *In* Proceedings Beltwide Cotton Prod. Res. Conf. National Cotton Council, Memphis, TN.

Hoffmann, W.C. 1999. Temporal degradation of ULV malathion under field conditions, pp. 1148-1150. *In* Proceedings Beltwide Cotton Prod. Res. Conf. National Cotton Council, Memphis, TN.

Igniffo, C.M. and O.F. Batzer. 1971. Microencapsulation and ultraviolet protectants to increase sunlight stability of an insect virus. *J. Econ. Entomol.* 64(4):850-853.

Jaques, R.P. 1968. The inactivation of the nuclear-polyhedrosis virus of *Trichoplusia ni* by gamma and ultraviolet radiation. *Can. J. Microbiology* 14(6):1161-1163.

Jones, R.G., J.W. Haynes, and J.E. Mulrooney. 1996a. Efficacy of malathion ULV on the cotton boll weevil under simulated cool temperature regimes, pp. 719-721. *In* Proceedings Beltwide Cotton Prod. Res. Conf. National Cotton Council, Memphis, TN.

Jones, R.G., D.A. Wolfenbarger, and O. El-Lissey. 1996b. Malathion ULV rate studies under boll weevil eradication program field conditions, pp.717-718. *In* Proceedings Beltwide Cotton Prod. Res. Conf. National Cotton Council, Memphis, TN.

Mulrooney, J.E., K.D. Howard, J.E. Hanks, and R.G. Jones, 1997. Application of ultra-low-volume malathion by air-assisted ground sprayer for boll weevil (Coleoptera: Curculionidae) control. *J. Econ. Entomol.* 90(2):639-645.

National Renewable Energy Laboratory. Golden, CO. URL: www.nrel.gov.

Shapiro, M. 1989. Congo red as an ultraviolet protectant for the gypsy moth (Lepidoptera: Lymantriidae) nuclear polyhedrosis virus. *J.Econ.Entomol.* 82(2):548-550.

Shapiro, M. 1992. Use of optical brighteners as radiation protectants for the gypsy moth (Lepidoptera: Lymantriidae) nuclear polyhedrosis virus. *J.Econ.Entomol.* 82(2):548-550.

Shapiro, M., and R. Argauer. 1995. Effects of pH, temperature, and ultraviolet radiation on the activity of an optical brightener as a viral enhancer for the gypsy moth (Lepidoptera: Lymantriidae) baculovirus. *J.Econ.Entomol.* 88(6):1602-1606.

Villavaso, E.J. J.E. Mulrooney, W.L. McGovern, and K. Howard. 1996. Lower dosages of malathion for boll weevil eradication, pp. 727-729. *In* Proceedings Beltwide Cotton Prod. Res. Conf. National Cotton Council, Memphis, TN.

Table 1. Boll weevil mortality (%) from ULV malathion/ UV protectants mixtures.

Treatment	Days after Treatment (DAT)*				
	0	1	3	6	10
PABA	98.3a	98.3a	91.7ab	93.3a	81.7a
Congo Red	100.0a	100.0a	100.0a	86.7a	79.7a
Fluorescent 28	98.3a	100.0a	96.7ab	85.0a	83.3a
ULV malathion only	91.7a	98.3a	80.0b	76.7a	28.3b
Check	6.7b	1.7b	11.7c	13.3b	3.3c

* Means in the same column for each date with the same letter are not significantly different at p=0.05, Duncan's multiple range test.

Table 2. Percent decrease of 0 DAT malathion residue found on cotton leaves treated with ULV malathion/UV protectant mixtures.

Treatment	Days after Treatment (DAT)			
	1	3	6	10
PABA	0.0	58.5	58.5	75.1
Congo Red	6.7	8.3	10.8	67.0
Fluorescent 28	13.6	24.3	39.5	68.8
ULV malathion only	0.0	2.1	74.8	59.1