

THE PERSISTENCE OF SELECTED INSECTICIDES USED IN WATER AND
IN WATER-OIL SPRAYS AS RELATED TO WORKER REENTRYC. L. Cole, ^{1/}, W. E. McCasland ^{2/}, and S. C. Dacus ^{2/}

ABSTRACT

Laboratory analyses were made of residues recovered from cotton leaves collected from plots treated with water and with water-oil sprays of selected insecticides. In 1984 plots were treated with fenvalerate and methyl parathion. In 1985 plots were treated with azinphosmethyl and cypermethrin. Initially residues were greater with the water formulations of azinphosmethyl and cypermethrin while they were higher with the oil formulations of fenvalerate and methyl parathion. Residues of azinphosmethyl and methyl parathion declined at a much faster rate than did those of cypermethrin and fenvalerate regardless of carrier. The addition of oil reduced the rate of insecticide loss when used with methyl parathion, azinphosmethyl and fenvalerate but had little effect when added to cypermethrin.

INTRODUCTION

An increase in activity of certain insecticides applied in oil formulations has been observed in the field as an enhanced control of cotton pests. Womack et al. (1985) showed that a soybean oil carrier was superior to water as a carrier for the control of bollworms in cotton. Treacy et al. (1985) reported enhanced control of boll weevils using oil formulations as compared to water formulations of oxamyl. Conversely, they reported reduced control of boll weevils using oil formulations as compared to water formulations of azinphosmethyl. Awad and Vinson (1968) reported that a greater amount of malathion was found in dead larvae from cotton leaves treated with an ultra-low volume formulation than in larvae from leaves treated with an emulsifiable concentrate.

Due to the possible increased pesticide residue in fields, and possible adverse effects upon workers reentering fields treated with oil formulations, a study was conducted to quantify insecticide residues of water-oil sprays as compared to conventional applications in water-only sprays.

MATERIALS AND METHODS

Chemical Application. Selected insecticides were applied to cotton fields in the Brazos River Bottom in Burleson County, Texas. Methyl parathion and fenvalerate were applied 25 July 1984. Azinphosmethyl and cypermethrin were applied 8 August 1985. Both tests were initiated when the plants were between 40 and 48 inches tall and mature bolls were present. No rainfall was recorded either year during the test period.

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Applications were made with a pawnee airplane equipped with 40 nozzles (core 45, orifice D-5) on the boom. The treatments, as given in Table 1, were applied to 10 acre plots. Special care was given to calibration of the aircraft and to preparing the spray materials. Otherwise, applications were made in the manner traditionally used for commercial application of insecticides to cotton fields.

Table 1. Treatments Applied to Cotton Plots.

| Year Treated | Treatment | Rate per acre (pt.) | | | |
|--------------|---------------------|---------------------|----------|--------|--------------|
| | | Insecticide | Crop Oil | Water | Total Volume |
| 1984 | Fenvalerate 2.4EC | 1/3 | 2 | 13 2/3 | 16 |
| | Fenvalerate 2.4EC | 1/3 | 0 | 15 2/3 | 16 |
| | Methyl Parathion 4E | 2 | 2 | 12 | 16 |
| | Methyl Parathion 4E | 2 | 0 | 14 | 16 |
| 1985 | Cypermethrin 2.5EC | 1/4 | 2 | 13 3/4 | 16 |
| | Cypermethrin 2.5EC | 1/4 | 0 | 15 3/4 | 16 |
| | Azinphosmethyl 2EC | 1 | 2 | 13 | 16 |
| | Azinphosmethyl 2EC | 1 | 0 | 15 | 16 |

Sampling. Care must be taken to keep residue samples as uniform and representative as possible. Attention must be given adequate replication, environmental factors such as moisture, and sample storage conditions (Iwata et al. 1977).

In this study, samples were taken at predetermined intervals of 24 and 48 h. Samples were taken from each of four replications of each treatment. Each sample consisted of whole, mature leaves collected away from terminals so as to avoid any new growth which occurred after treatment. Leaves were collected in a prescribed path across the swaths. In an effort to keep samples uniform, the same path was traversed for each sample on each collection date. The leaves were packed into quart canning jars, sealed and frozen for future analysis.

Analysis. Residue analyses were made at the Texas Department of Agriculture Laboratory in Brenham, Texas. Methyl parathion analysis was made according to the method of Luke et al. (1981). Ten grams of leaves were blended 4 min with 200 ml acetone and 50 ml water. A 100 ml aliquot was taken and partitioned once with 200 ml 50/50 dichloromethane/petroleum ether and twice with dichloromethane after 5 gm of NaCl was added to the aqueous phase. Each organic fraction was passed through anhydrous Na_2SO_4 into a Kuderna-Danish flask equipped with a 10 ml receiving tube. The organic solvents were evaporated to near dryness and three, 20 ml portions of acetone were added sequentially and taken to near dryness. The flasks were allowed to cool and the volume was adjusted to 10 ml with acetone. Samples, thus prepared, were ready for analysis for methyl parathion with no further clean-up.

Azinphosmethyl analysis was made according to the methods of Luke et al. (1981) with slight modifications. Twenty grams of leaves were weighed out into a blender jar and 20 ml distilled water added. The leaves were blended on medium speed for 4 min with 200 ml of acetone. A 50 ml aliquot was taken after filtration for the first 3 samples; all subsequent aliquots were 100 ml. The aliquot was partitioned once with 200 ml 50/50 mix of dichloromethane and petroleum ether and twice with dichloromethane after 5 grams of NaCl were added to the aqueous phase. Each organic fraction was passed through Na_2SO_4 into a Kuderna-Danish flask with 10 ml receiving tube. The organic fractions were evaporated to near dryness on a steam table and two, 20 ml portions of acetone added sequentially and

taken to near dryness each time. A third rinse consisted of 20 ml of hexane added to the organic fraction and taken to near dryness. The flask was allowed to cool and the volume was adjusted to 10 ml with hexane. The samples thus prepared were ready for analysis with no further clean-up.

Cypermethrin and fenvalerate analyses were made according to those recommended by Shell Development Company (Anonymous 1978) with only minor modifications. Ten grams of cotton leaves were blended 4 min with 200 ml 3:1 hexane isopropanol. The extract was then suction filtered through glass fiber filter paper and decanted into a 250 ml separatory funnel. The filtrate was partitioned three times with distilled water after which the aqueous phases were discarded. Six grams of Florisil were added to a reservoir column fitted with a glass wool plug and a layer of Na_2SO_4 (1-2 cm). Another layer (1-2 cm) of Na_2SO_4 was added to the top and the column was tapped vigorously to settle the material. The column was then washed with 50 ml of hexane. The hexane was drained until less than 1 ml remained at the top. A 50 ml aliquot of the organic phase was transferred to the column and drawn through. Fifty ml of 5% (v/v) ethyl acetate in hexane were added and drained into a 250 ml Phillips beaker. This fraction was concentrated on a steam table and the volume was brought up to 10 ml with hexane. The sample was then injected into the gas chromatograph.

Samples from each pesticide treatment were diluted as needed for gas chromatography. Each sample was injected twice, preceded and succeeded with a standard solution. Samples were quantitated by an external standard technique using areas generated with Nelson Analytical Chromatography software.

RESULTS AND DISCUSSION

Test 1. Insecticide residues recovered from cotton leaves collected from plots treated with methyl parathion plus crop oil were higher throughout the 5-day study than were residues collected from plots where no crop oil was added to the spray. On the 5th day, the oil plots had approximately three times as much residue as did the plots where no oil was used (Table 2). Residues recovered from plots treated with fenvalerate plus oil were initially higher than from plots where fenvalerate was applied with water alone. However, by the 5th day the residue from both plots were approximately the same.

Table 2. Residues Collected from Cotton Leaves Taken from Plots Treated with Water and with Water-Oil Sprays of Fenvalerate and Methyl Parathion.

| Year Treated | Insecticide | Days Post Treatment | Residue in ppm | |
|--------------|------------------|---------------------|---------------------------------------|-----------------------------------|
| | | | Water-Oil ($\bar{x} \pm \text{SE}$) | Water ($\bar{x} \pm \text{SE}$) |
| 1984 | Fenvalerate | 1 | 9.77 + 2.04 | 6.23 + 2.12 |
| | | 2 | 8.36 + 1.78 | 6.93 + 3.34 |
| | | 3 | 8.23 + 1.29 | 6.70 + 2.96 |
| | | 4 | 8.57 + 1.37 | 6.81 + 2.48 |
| | | 5 | 6.29 + 1.70 | 6.89 + 3.22 |
| 1984 | Methyl Parathion | 1 | 27.70 + 7.99 | 14.80 + 8.74 |
| | | 2 | 9.68 + 4.29 | 9.17 + 7.15 |
| | | 3 | 7.48 + 2.85 | 2.30 + 0.89 |
| | | 4 | 8.70 + 4.58 | 1.52 + 0.31 |
| | | 5 | 5.97 + 2.61 | 1.96 + 1.49 |

Test 2. When water and water-oil sprays of azinphosmethyl and cypermethrin were compared, greater residues were initially recovered from both compounds where no oil was added to the spray (Table 3). By the 5th day, the residue was about the same for both sprays. These data for azinphosmethyl were interesting in that they agreed with those data from Treacy et al. (1986) where they reported less mortality of boll weevils caged on plants treated with azinphosmethyl in water-oil sprays than on plants treated with azinphosmethyl and water alone.

In both the above tests, the longer residual of the pyrethroids as compared to the organophosphates is quite evident. This is so, regardless of whether or not crop oil was added to the formulation. The effects of adding oil to the insecticide sprays varied with the specific compound. The rate of insecticide loss was reduced when oil was added to azinphosmethyl, methyl parathion and cypermethrin. Adding oil to fenvalerate had little effect on the rate of insecticide loss.

Table 3. Residues Collected from Cotton Leaves Taken from Plots Treated with Water and with Water-Oil Sprays of Azinphosmethyl and Cypermethrin.

| Year Treated | Insecticide | Days Post Treatment | Residue in ppm | |
|--------------|----------------|---------------------|--------------------------------|----------------------------|
| | | | Water-Oil ($\bar{x} \pm SE$) | Water ($\bar{x} \pm SE$) |
| 1985 | Azinphosmethyl | 1 | 17.74 + 3.21 | 28.63 + 9.53 |
| | | 2 | 8.86 + 2.59 | 13.0 + 4.92 |
| | | 3 | 12.02 + 1.14 | 14.0 + 4.08 |
| | | 4 | 7.01 + 0.83 | 8.38 + 1.72 |
| | | 5 | 4.39 + 1.41 | 5.26 + 2.19 |
| | | 7 | 3.56 + 0.70 | 4.06 + 0.90 |
| 1985 | Cypermethrin | 1 | 6.32 + 2.34 | 12.93 + 5.31 |
| | | 2 | 7.63 + 1.19 | 10.48 + 3.08 |
| | | 4 | 5.73 + 2.85 | 9.47 + 2.52 |
| | | 6 | 5.80 + 1.95 | 5.74 + 2.09 |
| | | 8 | 6.24 + 3.14 | 5.47 + 2.70 |
| | | 10 | 4.26 + 1.50 | 6.35 + 1.45 |
| | | 12 | 4.42 + 2.51 | 4.21 + 2.17 |
| | | 14 | 5.49 + 3.99 | 3.47 + 2.13 |
| | | 16 | 3.40 + 1.57 | 3.03 + 1.43 |

LITERATURE CITED

- Anonymous. 1982. Gas liquid chromatographic determination of Pydrin residues in crops, animal tissues, soil and water. Pesticide Analytical Manual. Vol. 2, Sec. 180.379.
- Awad, T. M. and S. B. Vinson. 1968. The pick-up and penetration of ultra-low volume and emulsifiable concentrate malathion formulations by tobacco budworm larvae. J. Econ. Entomol. 61: 242-245.
- Iwata, Y., R. C. Spear, J. B. Knaak, and R. J. Foster. 1977. Worker reentry into pesticide-treated crops. 1. Procedure for the determination of dislodgeable pesticide residues on foliage. Bull. Environ. Contam. Toxicol. 6: 449-462.
- Luke, M. A., J. E. Froberg, G. M. Doose, and H. T. Masumota. 1981. Improved multiresidue gas chromatographic determination of organophosphorous, organonitrogen, and organohalogen pesticide in produce, using flame photometric and electrolytic conductivity detectors. J. Assoc. Offic. Anal. Chemists 64: 1187-95.

- Treacy, M. F., J. H. Benedict, and M. H. Walmsley. 1985. Effects of emulsified oils on residual toxicity of Vydate and Guthion to the boll weevil. Proc. Beltwide Cotton Conference. New Orleans, LA. pp. 189-191.
- Treacy, M. F., J. H. Benedict, and K. M. Schmidt. 1986. Toxicity of insecticide residues to the boll weevil: Comparison of ultra-low volume/oil vs. conventional/water and water-soil sprays. Southwest. Entomol. Suppl. No. 11: 19-24.
- Womack, C. L., J. P. McCaa, M. S. Schuster, and M. T. Parker. 1985. Mineral and vegetable oil effects on insects and as carriers of pesticides. Proc. Beltwide Cotton Conference. New Orleans, LA. pp. 186-187.

Addendum: once-refined cottonseed oil was used in this study