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Effect of Toxaphene, Camphene, and Cedar Oil on Methyl Parathion Residues on Cotton

W. S. Bigley, F. W. Plapp, Jr., R. L. Hanna, and J. A. Harding

Texas Agricultural Experimental Station, Texas A&M University, College Station, TX 77843

For many years methyl parathion (MP) has been the major insecticide applied to cotton in the United States. Often, MP has been applied in combination with toxaphene (TOX) and evidence has been obtained (NEMEC et al. 1968, McGARR et al. 1970) that MP:TOX combinations are more effective than MP alone for the control of Heliothis pests of cotton. Since there is widespread resistance to TOX in Heliothis and other cotton insect pests (ADKISSON 1967) it is possible that the major present usefulness of TOX lies not in its insecticidal properties, but in its effects on the persistence of MP. Evidence that TOX increases the persistance of MP residues on cotton in Arizona has been reported (WARE et al. 1975, 1978, 1979, 1980).

A recent report (HOOPER et al. 1979) has suggested that TOX is mutagenic. Since TOX may soon be unavailable for field use, we undertook tests to quantitate the effect of TOX on MP residues under Texas conditions and also, to determine if there are substitutes that might replace TOX as an MP additive.

MATERIALS AND METHODS

Materials tested were MP applied alone and in combination with TOX, camphene, or cedar oil. MP and TOX were EC formulations obtained commercially. Practical grade camphene and cedar oil (extract of eastern redcedar, Juniperus virginiana) were obtained commercially and prepared as 6 lb/gal EC formulations with xylene and Tween 20 to be comparable with 6 lb/gal TOX. TOX, camphene, or cedar oil were tank mixed with 4 lb/gal MP to obtain desired ratios.

Tests were conducted in the Rio Grande Valley near Weslaco, TX and in central Texas near College Station. Insecticide combinations tested at Weslaco and College Station are listed in Tables 1 and 2, respectively. At Weslaco, 0.94 ha plots of Stoneville 213 cotton about 100 cm tall were arranged in a randomized complete block design and replicated 3 times. The test area was irrigated prior to treatment and no rainfall occurred during the experiment. The plots were treated by air 3 times in June, 1978 at 4 day intervals. At College Station, 0.04 ha plots of 100 cm tall CAMD-E cotton were arranged in a

Address correspondence to:
Frederick W. Plapp, Jr.
Department of Entomology
Texas A&M University
College Station, Texas 77843

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randomized complete block design and replicated 4 times. Each plot consisted of 12 rows, 33 m long. Sprays were applied at the rate of 16 liters/ha with an 8 row Hahn Hi Boy sprayer modified with a second engine and pump and 8 40 l tanks for spraying small experimental plots. Insecticides were sprayed with #3 hollow cone nozzles with the nozzles mounted 50 cm apart on a boom maintained at least 20 cm above the tallest plants. Spray pressure was 117 kg/cm^2. 5 applications were made from 28 June to 16 July, 1978 and no rain fell during the experiment.

Leaf samples were collected for residue analysis. At Weslaco, 50 fully expanded upper leaves were collected from the middle rows of each plot at each sampling time and immediately placed in a refrigerated ice chest. They were held at -18°C until shipment to College Station. Residues were determined from 24 2.5 cm discs punched from randomly selected leaves of each sample.

At College Station 32 upper leaves were collected from the middle rows of each plot. These were held on ice and transported to the laboratory where 3 2.5 cm discs were punched from each leaf. Two 24 randomly selected disc samples were taken for analysis.

Extracts of surface insecticide residues were prepared by washing the leaf discs with 35 ml distilled water in a flask in a reciprocating shaker for 1 h. The discs were reextracted 30 min. with more water. Pooled water samples were extracted 2 X with 50 ml petroleum ether, dried with sodium sulfate, concentrated under N_2 gas and placed in glass vials in a freezer until GLC analysis for MP residues.

Samples were analyzed for MP by GC using a phosphorus detector and a 1.9 m glass column (0.3 cm I.D.) packed with 10% DC-200 on Chromosorb W-HP (80/100 mesh). The column oven was maintained at 195°C and the injector port at 225°C. Carrier gas was N_2 at a flow rate of 70 cc per min.

The same extracts were used for TOX analyses after basic hydrolysis by a modification of the Gomes (1977) procedure. Extracts were concentrated to near dryness with N_2, 10 ml 9N methanolic KOH added, and the samples heated 1 h in sealed vials at 50°C. After cooling the samples were partitioned with petroleum ether and water. Petroleum ether extracts, reduced to small volume with N_2, were spotted on TLC plates (Brinkmann Instruments, Inc., precoated with Sil G-25 UV 254) and developed with 9:1 benzene:acetic acid to a height of 10 cm. After air drying a spot visible at R_f 0.9 under UV light was scraped from the plates and eluted with 10 ml acetone. The eluate was concentrated to dryness with N_2 and the residue dissolved in 10 ml petroleum ether. Analysis was by EC GC equipped with a 3.3 m glass column (0.3 cm I.D.) packed with Chromosorb W-HP 80/100

mesh with 2% SE-30 and 3% QF-1 as the stationary phase. Temperatures were 212°C for the column oven, 225°C for the injector port and 280°C for the detector.

GC analyses showed 1 major and several minor peaks with a total retention time of about 4 min. A linear response was obtained over a range of 0.001-100 ng TOX. Since base treated preps of known TOX as well as residue extracts gave similar GC patterns, only the major peak was used for quantitating TOX residues.

RESULTS

Data on MP residues on cotton at Weslaco are shown in Table 1. Values given are averages of samples collected after each of 3 aerial applications of insecticide. Initial MP residues from the MP only and MP + camphene treatment averaged slightly less than 1 ug/cm^2 and declined to very low levels by 23 h. Initial MP residues were about 50% higher from the MP + TOX treatment and declined at a slower rate. At 23 h, residues from this treatment were greater than for any other treatment at 4-6 h. MP residues from the MP + cedar oil treatment were initially as great as those from MP + TOX, but declined more rapidly.

TABLE 1

Surface residues of methyl parathion (MP) applied alone and with adjuvants to cotton by aerial application at Weslaco, TX.

Treatment	Dose (kg/ha/ application)	MP in ug/cm^2 on cotton leaves ± S.D. 2-3 h	4-6 h	23 h
MP only	1.12	0.95 ± 0.30	0.31 ± 0.14	0.17 ± 0.11
MP + Toxaphene	1.12+1.12	1.47 ± 0.68	0.75 ± 0.10	0.46 ± 0.18
MP + Camphene	1.12+1.12	0.88 ± 0.55	0.32 ± 0.08	0.14 ± 0.01
MP + Cedar Oil	1.12+1.12	1.41 ± 0.68	0.45 ± 0.22	0.22 ± 0.07

Data on MP residues at College Station are summarized in Table 2. Values are averages of samples taken following each of 5 treatments. Generally, residues were lower from these applications made with ground equipment than from the aerial applications at Weslaco. We have no explanation for this difference.

Initial MP residues of 0.38 ug/cm^2 were obtained with the MP only treatment. These were substantially dissipated by 4 h posttreatment. All 3 adjuvants, TOX, camphene, and cedar oil,

resulted in higher initial MP residues than the MP only treatment and camphene and cedar oil were as good or better in increasing these residues as TOX. MP residues dissipated rapidly for all treatments, but apparently at a slower rate for MP + TOX than for the other combinations. The higher dose of TOX, 2.24 kg/ha, was more effective than 1.12 kg/ha in increasing initial MP residues and at maintaining them through 4 h posttreatment.

TABLE 2

Surface residues of methyl parathion (MP) applied alone and with adjuvants to cotton by ground application at College Station, TX.

Treatment	Dose (kg/ha/ application)	MP in ug/cm^2 on cotton leaves ± S.D. 0.25 h	4 h	8 h	24 h
MP only	1.12	0.38±0.19	0.05±0.02	0.06±0.02	<0.10
MP + Toxaphene	1.12+1.12	0.57±0.44	0.18±0.22	0.07±0.01	"
MP + Toxaphene	1.12+2.24	1.07±0.68	0.46±0.32	0.07±0.06	"
MP + Camphene	1.12+1.12	0.98±0.21	0.09±0.05	0.03±0.02	"
MP + Cedar Oil	1.12±1.12	0.87±0.33	0.17±0.11	0.17±0.17	"

TOX was significantly more persistent than MP on cotton leaves in the College Station tests (Table 3). Residue half life was at least 8 h in all cases and concentrations greater than 0.1 ug/cm^2 were still present at 48 h posttreatment. Initial surface residues of TOX were higher for the TOX only treatment at 1.12 kg/ha then for TOX + MP where both chemicals were applied at this rate and this difference persisted throughout the experiment.

TABLE 3

Surface residues of toxaphene (TOX) applied alone and with methyl parathion to cotton by ground application at College Station, TX.

Treatment	Dose (kg/ha/ application)	TOX in ug/cm^2 on cotton leaves 0.25 h	4 h	8 h	24 h	48 h
TOX only	1.12	0.45	0.27	0.25	0.15	0.16
TOX + MP	1.12+1.12	0.19	0.22	0.20	0.08	0.11
TOX + MP	2.24+1.12	0.54	0.51	0.29	0.31	0.12

DISCUSSION

MP is a nonpersistent insecticide on cotton. The results demonstrate clearly its persistence can be increased by combining it with TOX and to a lesser extent, camphene or cedar oil. In this respect, results agree very well with the Arizona tests of WARE et al. (1975, 1978, 1979, 1980).

A second finding is that initial residues of MP may be increased by the addition of appropriate adjuvants. This was shown with all adjuvants in the College Station tests and with TOX and cedar oil at Weslaco. The nature of the effect is not known, but is probably physical, i.e. competition between the chemicals for uptake by the leaves.

TOX is a much more persistent insecticide on cotton than MP. However, when it was combined with MP, lower surface residues were found than for TOX only treatments. These results suggest that MP in someway facilitates the uptake of TOX by cotton leaves.

Overall, the data suggest the beneficial effects of TOX may simply be due to a physical effect of increasing surface residues of MP. If this is true, it should be possible to produce the effect with substitutes of appropriate properties. In this way, the benefits of TOX could be obtained without the hazards associated with its use.

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REFERENCES

ADKISSON, P. L.: J. Econ Entomol. 60, 788 (1967).

HOOPER, N. K., B. N. AMES, M. A. SALEH, J. E. CASIDA: Science 205, 591 (1979).

McGARR, R. L., H. T. DULMAGE, D. A. WOLFENBARGER: J. Econ. Entomol. 63, 1357 (1970).

NEMEC, S. J., P. L. ADKISSON, H. W. DOROUGH: J. Econ. Entomol. 61, 209 (1968).

WARE, G. W., B. ESTESEN, W. P. CAHILL: Bull. Environ. Contam. Toxicol. 14, 606 (1975).

WARE, G. W., B. ESTESEN, N. A. BUCK: Bull. Environ. Contam. Toxicol. 20, 24 (1978).

WARE, G. W., B. J. ESTESEN, N. A. BUCK: Bull Environ. Contam. Toxicol. 21, 657 (1979).

WARE, G. W., T. F. WATSON, B. ESTESEN, N. A. BUCK: J. Econ. Entomol. 73, 15 (1980).

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