## Effects of Toxaphene on the Residual Life of Methyl Parathion on Cotton<sup>1</sup>

G. W. Ware, B. J. Estesen, and N. A. Buck University of Arizona, Tucson, Ariz. 85721

After the cancellation of DDT registrations on cotton by the EPA in 1973, various emulsifiable concentrate mixtures of DDT-toxaphene were replaced with toxaphene-methyl parathion formulations. These formulations contained 4 or 6 lb of toxaphene and 2 or 3 lb of methyl parathion per gallon. Application rates were usually 2 or 3 lb of toxaphene and 1 lb of methyl parathion per acre.

The rationale for this mixture apparently hinged on the efficacy of the original DDT-toxaphene mixture used against the cotton boll weevil. The value of this combination faded after 2 or 3 years of use when the boll weevil became resistant to it. This observed synergistic quality did not extend to other cotton pests.

Various qualities have been attributed to toxaphene-methyl parathion by growers and agricultural fieldmen alike, including enhanced insect control through the influence of toxaphene as a protective screen against the sun's ultraviolet, its effect as a sticker or adhesive, thus preventing washing off by rain, or as a protective film against volatility. There are few data to support these testimonials despite the combination's availability for more than 10 years.

It was thus the purpose of these experiments to determine the influence of toxaphene in various ratios on methyl parathion residues on cotton.

## METHODS AND MATERIALS

The test plots were located in a 6.5 ha block of Stoneville 256 short staple cotton on the Arizona Agricultural Experiment Farm, Marana, Arizona. The plots were treated on August 27, 1977, when the cotton averaged 108 cm in height. Each plot consisted of 4 rows, with 102 cm spacing, 30.5 m long. The sprays were

<sup>1</sup> Contribution to Regional Project W-45, "Residues of Pesticides and Related Chemicals in the Agricultural Environment--Their Nature, Distribution, Persistence, and Toxicological Implications." University of Arizona Agricultural Experiment Station No. 2855.

applied at the rate of 122 L/ha, at 4.0 km/h and 276 kPa. The spray rig was a manually-drawn spray apparatus, designed to treat 2 rows at a time, using 3 DC-2-13 Spraying System nozzles per row. Pressure was maintained from a small 1.37 kg CO<sub>2</sub> tank using a single stage regulator.

Toxaphene EC (8 1b AI/gal) and methyl parathion EC (7.5 1b AI/gal) were premeasured in the laboratory and carried to the field in labeled jars. Six plots were treated at the rate of 1.14 kg/ha of methyl parathion plus toxaphene at 0, 0.28, 0.57, 1.14, 2.28 and 4.56 kg/ha.

Maximum and minimum temperatures during the study were: Aug. 22,  $36.7^{\circ}$  -  $23.3^{\circ}$ ; Aug. 23,  $38.3^{\circ}$  -  $21.1^{\circ}$ ; Aug. 24,  $38.9^{\circ}$  -  $23.3^{\circ}$ ; Aug. 25,  $40.0^{\circ}$  -  $21.1^{\circ}$ ; and Aug. 26,  $38.3^{\circ}$  -  $20.0^{\circ}$  C. No precipitation occurred during the study.

Triplicate leaf samples were collected in each treated and control plot at 0, 24, 48, 72 and 96 h, after treatment. Each sample consisted of ca 150 2.54-cm diameter leaf punches made singly and consecutively from the top, middle and bottom portions of plants in all 4 rows. These were returned to the field laboratory where they were counted into 3 100-disc samples and extracted.

Samples were extracted by shaking with 100 ml of redistilled benzene for 1 min. Extracts were decanted into 8-oz bottles, solvent level marked, maintained on ice until they were returned to the laboratory, and then held at 4.4° C.

Methyl parathion and paraoxon were measured by gas chromatography using a MicroTek MT-220 equipped with a flame photometric detector; a 1.22 m 4 mm I.D. Pyrex column packed with 1.5% OV-17 and 2% QF-1 on 100/120 mesh Chromosorb W (H.P.) was used. Quantitation was by peak height. Carrier gas flow was 60 mL/min  $N_2$  and column temperature was  $200^{\circ}$ C. No cleanup was applied to any of the samples.

## RESULTS AND DISCUSSION

The results in Table 1 are expressed as  $\mu g$  of methyl parathion and methyl paraoxon per cm² of upper leaf surface ( $\mu g/\text{cm}^2$ ), and represent an average of the 3 replicated samples. These data show that the addition of 0.57 kg or more of toxaphene per 1.14 kg of methyl parathion increases the initial deposit of methyl parathion by approximately 10% per kg of added toxaphene over methyl parathion alone. Additionally, 1.14 kg or more of toxaphene per 1.14 kg of methyl parathion increases the 24-h residue by approximately 3-fold over methyl parathion alone. The influence of toxaphene on the 48-h residues is evident but probably insignificant relative to efficacy. Similar results have been observed by WARE et al. (1975, 1978a, 1978b) when toxaphene was

Methyl Parathion and Methyl Paraoxon Residues  $(\mu g/cm^2)^{2a/2}$  on the Upper Surfaces of Cotton Leaves as Influenced by Different Ratios of Toxaphene. TABLE 1.

Methyl Parathion + Toxaphene 1.1444.56 kg/ha	Methyl Para- oxon	0.010	0.019	900.0	0.003	0.002
	Methyl Para- thion	2.70	0.89	0.41	0.17	0.13
Methyl Parathion Toxaphene 4+2.28 kg/ha	Methyl Para- oxon	0.008	0.013	0.007	0.003	0.002
Methyl Parathion + Toxaphene 1.14+2.28 kg/ha	Methyl Para- thion	2.20	0.77	0.51	0.11	60.0
Methyl Parathion + Toxaphene 1.14+1.14 kg/ha	Methyl Para- oxon	0.012	0.008	0.003	0.001	<0.001
	Methyl Para- thion	2.40	0.61	0.13	90.0	0.03
Methyl Parathion + Toxaphene 1.14+0.57 kg/ha	Methyl Para- oxon	0.007	0.009	0.003	0.002	<0.001
Methyl Parathi + Toxaph	Methyl Para- thion	2.10	0.29	0.10	0.07	0.03
lyl hion phene 8 kg/ha	Methyl Para- oxon	900.0	0.008	0.004	<0.001	<0.001
Methyl Parathion + Toxaphene 1.14+0.28 kg/ha	Methyl Para- thion	1.60	0.19	0.07	0.04	0.03
Methyl Parathion 1.14 kg/ha	Methyl Methyl Para- Para- thion oxon	0.007	0.011	900.0	0.002	<0.001
Methyl Parathi 1.14 kg/		1.80	0.27	0.09	0.03	0.02
	Hours	0	24	48	72	96

 $\overline{a}^{\prime}$  Residue data corrected to reflect variations in rate of manual application.

added at the rate of 2:1 to methyl parathion. In these instances the initial methyl parathion residue was doubled with toxaphene, while the 24-h residue was some 10-20 fold of the methyl parathion alone. Methyl parathion also has a longer half-life when applied undiluted than diluted with water. SAINI and DOROUGH (1970) found that methyl parathion as a 3.5% aqueous solution at 1.14 kg/ha had a residual half-life of 4 h compared to that of the ultra low-volume application of 12 h under identical growth chamber conditions.

From these data, it is apparent that toxaphene increases both the deposition or initial residue and the residual life of methyl parathion on cotton foliage. Further, the 0.28 and 0.57 kg additions seem to offer little value while the 1.14 and 2.28 kg levels have substantial influence on its residual life. Of these, the 1.14 kg rate appears to be the optimum for residual efficiency of methyl parathion.

The role of toxaphene, as a residual extender has not been identified. However, it is thought to be a solvent of low volatility which reduces the volatility of methyl parathion as well as reducing its hydrolytic and photolytic decomposition. Despite its weak contribution insecticidally, toxaphene undoubtedly serves a useful purpose in certain insecticide formulations by increasing initial deposit and extending the residual lives of chemically unstable or highly volatile insecticides.

## REFERENCES

- NASH, R. G., M. L. BEALL, JR., and W. G. HARRIS: J. Agric. Food Chem. 25, 336 (1977).
- SAINI, M. L. and H. W. DOROUGH: J. Econ. Entomol. 63, 405 (1970).
- WARE, G. W., B. J. ESTESEN and W. P. CAHILL: Bull. Environ. Contam. Toxicol. 14, 606 (1975).
- WARE, G. W., B. J. ESTESEN and W. P. CAHILL: Dislodgable Insecticide Residues on Cotton (1975). Bull. Environ. Contam. Toxicol. (In Press), (1978a).
- WARE, G. W., B. J. ESTESEN and N. A. BUCK: Dislodgable Insecticide Residues on Cotton (1976). Bull. Environ. Contam. Toxicol. (In Press), (1978b).