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RESIDUES OF MALATHION AND METABOLITES IN AND ON THE COTTON LEAF VS. TOXICITY TO THE BOLL WEEVIL

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Abstract

Malathion was applied at 12 and 16 oz [A.I.]/a to cotton near Mercedes, TX, in 1995 and sampled on 0, 2, 4 and 6 d posttreatment to determine residues of malathion, malaoxon, and iso-malathion. Residues were then compared to determine toxicity to boll weevil, *Anthonomus grandis* Boheman. Residues of malathion comprised 99% of the leaf washes and 100% of the leaf homogenates. Malaoxon was found in one leaf wash sample of a leaf collected on 0 d from cotton sprayed with the low use rate. Iso-malathion was not found in any sample. Residues of 2.43 to 13.63 ppm malathion killed 100% of the weevils on d 0 and 2. Residues of 1.55 to 1.99 ppm killed 89% to 90% of the boll weevils on d 4 and 0.5 to 1.26 ppm killed 72% to 81% of the boll weevils on d 6.

Introduction

Ultra-low volume applications of technical malathion have been made for the past 24 years against the boll weevil in the eradication programs in the United States of America. Wolfenbarger and McGarr (1971) determined quantities of malathion on and in the leaf. Information on residues of malathion from washes of the cotton leaf was shown by Wolfenbarger and McGarr [1971] and Mulrooney et al. [1997).

Wolfenbarger and McGarr (1971) were the first to show that water could physically remove residues of malathion from the leaf surface. Mulrooney et al. (1997) determined residues of malathion from the leaf surface and described methods of analysis used here.

Malaoxon is formed by oxidation following the removal of the sulfur atom on the phosphorus atom of malathion. Iso-malathion is a rearrangement compound formed when malathion is exposed to excessive temperatures during the synthesis process. It is not formed in samples of leaf washes nor homogenates of cotton leaves. Metabolites of malathion were not determined (Wolfenbarger and McGarr 1971 and Mulrooney et al. 1997) from cotton leaves following applications of technical malathion.

In 1995 an experiment was conducted near Mercedes, TX, in the Lower Rio Grande Valley to determine residues of malathion, malaoxon and iso-malathion on the leaf surface with washes of water and the homogenates of the cotton leaf. Residues were taken on 0, 2, 4 and 6 d following a single application of malathion at 12 and 16 oz (AI)/a. The mortalities of boll weevil from leaves sampled on the same d were compared to the residues.

Materials and Methods

Residues of malathion (>95% purity), malaoxon (succinic acid, (dimethylphosphinyl) with diethyl ester of 96.7% purity) and iso-malathion, (succinc acid, mercaptodiethylester, S-ester 0,S-dimethylphosphorodithioate of 97.3% purity) were determined from leaf washes and leaf homogenates. Compounds were analyzed with an H-P gas liquid chromatograph with a flame photometric detector sensitive to phosphorus [Mulrooney et al. 1997). Standards of malaoxon, malathion and iso-malathion showed a retention time (RT) of 4.900, 5.397 and 6.112 minutes, respectively, at 0.625 ppm. Areas (150 pA) of peaks at this concentration were 854.75, 1602.07 and 533.93 for malaoxon, malathion and iso-malathion, respectively. Solvents used to extract and dilute samples were nanograde quality.

Technical malathion was applied May 4, 1995, by airplanes used in the eradication program [Jones et al. 1996) to 10 fields near Mercedes, TX. Five of the fields were treated with 12 oz (A.I.)/a and five were treated with 16 oz (A.I.)/a.

From each of the 10 fields a leaf (third leaf from the top which was the same location used for the bioassay) from two different plants exposed to the spray of technical malathion were collected on 0, 2, 4 and 6 d. Each leaf was placed in 100 ml deionized water in glass bottles, capped and swirled for 10 to 15 s. The water was then decanted into another bottle and capped. Bottles of the water wash and the leaf for homogenization were returned to the USDA-ARS laboratory at Weslaco and frozen. Bottles were then sent to the USDA-ARS laboratory in Stoneville, MS, for analysis.

At the Stoneville laboratory 10 ml of water wash of each leaf were placed in 10 ml hexane. Hexane was used to extract malathion and malaoxon from the wash. Each frozen leaf was thawed and weighed. Each leaf was first washed with ethanol (10 ml) and then homogenized in ethanol (50 ml) for 3 min and the volumes were combined. The 60 ml of ethanol was then mixed with 60 ml hexane in a separatory funnel and shaken for 10 m. A five ml aliquot of hexane was taken from the extraction and reduced to one ml by a slow stream of prepurified nitrogen. Microliter volumes from the ml was used for analysis.

Residues of malathion and malaoxon in the leaf washes and homogenates were quantified as ppm. Peak areas of these two compounds were used to quantify concentrations for each sample and standard. Peaks of each insecticide with RT <2.0% the RT of the standard were used to quantitate malathion and malaoxon.

Residues for leaf homogenate and leaf wash of residues for malathion and malaoxon were determined as mean of two leaves in each of five replications (=fields) of each rate and d of sampling. Then the difference of residue (lowest and greatest ppm) and the percentage of residue on the leaf surface were determined.

Results and Discussion

Residues of malathion and malaoxon were determined following the first application of technical malathion at 12 and 16 oz (AI)/a on 0, 2, 4 and 6 d (Table 1). Water washes of cotton leaves removed >45% of malathion to four d following application. Six d after the first application >70% of malathion was removed with the wash. The remaining percentage of malathion was removed from the leaf homogenate with hexane.

Boll weevil mortality was 100% on leaves collected at 0 and 2 d after application. Mean total (leaf wash and homogenate) residues of malathion and malaoxon ranged from 2.44 to 13.63 ppm malathion. Four d following application residues of 1.55 to 1.99 ppm malathion killed 89 to 90% of the boll weevils. Six d following application residues of 0.5 ppm malathion killed 72%, while residues of 1.26 ppm killed 81% of the boll weevils.

Residues of malaoxon were determined because it is an expected metabolite in and on cotton leaves. Malaoxon was determined from only one sample of leaf wash on d 0 at the 12 oz rate of malathion; mean residues were 0.023 ppm. Not enough malaoxon was present to account for any toxicity to the boll weevil. Residues of malathion were >99.6% on 0 d than shown for malaoxon. No iso-malathion was found on any sample, therefore it was not present in the technical applied to the field. Malathion residues caused all of the toxicity to the boll weevil.

Wolfenbarger and McGarr (1971) showed, in a study to control lepidopteran pests, that 88% to 95% of technical malathion was removed with water washes of cotton leaves at 40 oz (AI)/a on 0 d following the first, second and fourth application. At 20 oz (AI)/a leaf washes removed 73% to 88% on 0 d following the same applications.

Mulrooney et al. (1997) showed residues of malathion applied at 20 oz (AI)/a from cotton leaves following washes with ethanol as 16.18 and 7.47 µg/cm² 0 and 2 d post treatment Mortalities were 100%. We presume that water and ethanol washes would remove equal concentrations of malathion. Wolfenbarger and McGarr (1971) determined concentrations of malathion applied at 20 oz (A)/a on the same days and they ranged from 0.05 to 3.02 µg/cm² following the wash. Residues found by Wolfenbarger and McGarr (1971) were >60% than found by Mulrooney et al. (1997). Wolfenbarger and McGarr (1971) showed that washes with water and washes with chloroform on individual leaves removed equal quantities of malathion.

References

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Table 1. Residues of malathion in leaf wash and leaf homogenates of cotton. Mercedes, TX. 1995.

Age Residue (d)	Residues Malathion (ppm)	Range	Leaf Wash (%)
	12 oz		
0	10.01	11.37	50
2	2.43	5.15	87
4	1.55	2.92	69
6	0.5	0.99	22
	16 oz		
0	13.63	31.68	80
2	8.85	22.13	84
4	1.9	5.03	46
6	1.26	2.36	29