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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF PREVENTION,
PESTICIDES AND
TOXIC SUBSTANCES

August 15, 2001

Memorandum

SUBJECT: Review of *Dissipation of Dislodgeable Foliar Methyl Parathion Residues Following Application of PENNCAP-M® Microencapsulated Insecticide to Cotton* (MRID No. 452697-02)

FROM: Renee Sandvig, Environmental Protection Specialist Renee Sandvig 8/20/01
Reregistration Branch II
Health Effects Division (7509C)

THRU: Al Nielsen, Branch Senior Scientist A Nielsen 8/20/01
Reregistration Branch II
Health Effects Division (7509C)

TO: Laura Parsons, Chemical Review Manager
Reregistration Branch I
Special Review and Reregistration Division (7508C)

DP Barcode: D270867

Pesticide Chemical Codes: 053501

EPA MRID Numbers: 452697-02

Attached is a review of the dislodgeable foliar residue data submitted by Cerexagri, Inc. (formerly Elf Atochem North America, Inc.). This review was completed by Versar, Inc. on February 12, 2001, under supervision of HED. It has undergone secondary review in the HED and has been revised to reflect Agency policies.

Executive Summary

The data collected reflecting the dissipation of Methyl parathion from leaf surfaces of treated cotton meet most of the criteria specified in the U.S. Environmental Protection Agency's (US-EPA) OPPTS Series 875, Occupational and Residential Exposure Test Guidelines, Group B: Postapplication Exposure Monitoring Test Guidelines, 875.2100, Foliar Dislodgeable Residue Dissipation. The data will be considered in future methyl parathion REDs.

Summary

The insecticide methyl parathion was applied to cotton plants in three geographical locations: California, Louisiana, and Texas. Cotton plants were treated with PENNCAP-M® Microencapsulated Insecticide, containing approximately 20.9 percent methyl parathion as the active ingredient (a.i.). The product is a flowable formulation consisting of a water suspension of polymeric-type microcapsules. The study was conducted to determine the residue levels of methyl parathion and two metabolites/degradation products, methyl paraoxon and 4-nitrophenol, that could be dislodged from cotton foliage following four ground spray applications of the test substance, each at an application rate of 1.0 pounds active ingredient (ai) per acre.

At each of the test sites, the maximum average corrected methyl parathion dislodgeable foliar residue (DFR) occurred immediately after the fourth application (2.12, 3.24, and 3.17 $\mu g/cm^2$ in California, Louisiana, and Texas respectively). The maximum average corrected methyl paraoxon DFR occurred 8-12 hours after the fourth application (0.0387, 0.0465, 0.0615 $\mu g/cm^2$ in California, Louisiana, and Texas respectively). The maximum average uncorrected 4-nitrophenol residue occurred on the day prior to the second application in Texas and Louisiana (0.0151 and 0.0137 $\mu g/cm^2$ respectively) while all values were <LOQ in California. The average corrected methyl parathion DFR declined to <LOQ (0.01 $\mu g/cm^2$) at the following times after the fourth application: at Day 14 (California), Day 7 (Louisiana and Texas). The average corrected methyl paraoxon DFR declined to <LOQ after the fourth application at Day 7 (California), Day 2 (Louisiana), and Day 3 (Texas).

Since methyl parathion and methyl paraoxon are assumed to have the same toxicity, the their DFR values were averaged and then added together before running a regression analysis. Half of the LOQ value was used for the first LOQ value found in a series of LOQ values. The calculated dissipation half-lives and R2 values were as follows for the combined residues:

- California - 1.6 days (R^2=0.98)
- Louisiana - 0.72 days (R^2=0.93)
- Texas - 0.76 days (R^2=0.99)

Conclusions

The study was in compliance with the major technical aspects of OPPTS Series 875 guidelines. There were issues and limitations of the data identified below.

- The leaf punch sampling approach was not thoroughly discussed.
- Information on tank mix analysis was not provided in the study report.

MEMORANDUM

TO: Renee Sandvig

cc: 1000.001-01
Al Nielsen
Margarita Collantes

FROM: Marit Espevik/Susan Anderson

DATE: February 12, 2001

SUBJECT: Review of *Dissipation of Dislodgeable Foliar Methyl Parathion Residues Following Application of PENNCAP-M® Microencapsulated Insecticide to Cotton* (MRID No. 452697-02)

This report reviews *Dissipation of Dislodgeable Foliar Methyl Parathion Residues Following Application of PENNCAP-M® Microencapsulated Insecticide to Cotton*, submitted by Cerexagri, Inc. (formerly Elf Atochem North America, Inc.). A summary of the study as well as its compliance with the U.S. Environmental Protection Agency's (US-EPA) OPPTS Series 875, Occupational and Residential Exposure Test Guidelines, Group B: Postapplication Exposure Monitoring Test Guidelines, 875.2100, Foliar Dislodgeable Residue Dissipation is provided. The following information may be used to identify the study:

Title:	*Dissipation of Dislodgeable Foliar Methyl Parathion Residues Following Application of PENNCAP-M® Microencapsulated Insecticide to Cotton*, 360 pages
Sponsor:	Rodney Bennett Cerexagri, Inc. (formerly Elf Atochem North America, Inc.) Agrochemicals Division 2000 Market Street, 21st Floor Philadelphia, PA 19103-3222
Performing Laboratories: (Field Study)	David Ennes Research For Hire, Inc. 1696 South Legget Street Porterville, CA 93257 Nelson Prochaska R & D Research, Inc 7033 Highway 103 Washington, LA 70589 Mike Phillips South Texas Ag Research Benson Loop Road Uvalde, TX 78802
Analytical Laboratories:	Frances Brookey Morse Laboratories, Inc. 1525 Fulton Avenue Sacramento, CA 95825
Author:	Tommy R. Willard, Ph.D. American Agricultural Services, Inc. 404 E. Chatham Street Cary, NC 27512
Report Date:	August 23, 2000
Identifying Codes:	MRID # 452697-02, Laboratory Project Number: KP-2000-01.

Executive Summary

This report reviews a dislodgeable foliar residue (DFR) study submitted by Elf Atochem North America, Inc. The insecticide methyl parathion was applied to cotton plants in three geographical locations: California, Louisiana, and Texas. Cotton plants were treated with PENNCAP-M® Microencapsulated Insecticide, containing approximately 20.9 percent methyl parathion as the active ingredient (a.i.). The product is a flowable formulation consisting of a water suspension of polymeric-type microcapsules. The study was conducted to determine the residue levels of methyl parathion and two metabolites/degradation products, methyl paraoxon and 4-nitrophenol, that could be dislodged from cotton foliage following four ground spray applications of the test substance, each at an application rate of 1.0 pounds active ingredient (ai) per acre.

Cotton leaf punch samples were collected from treated and control plots in Porterville, California (June 5-August 2, 2000), Washington, Louisiana (May 11-July 8, 2000), and Uvalde, Texas (May 6-July 3, 2000). The sampling was performed the day prior to and the day following the first three applications, prior to the fourth application, immediately after the fourth application, 8-12 hours after the fourth application, 1 day after the fourth application, 2,3,4 (Texas and Louisiana) or 5 (California), 7,10,13,14 (California and Texas sites), 21,28,35, and 42 days after the fourth application. A Birkestrand leaf punch sampler with a 1.0 inch punch diameter was used to collect 40 leaf discs per sample. At each field test site, leaf punch samples were collected from three subplots in the treated plot. A single leaf punch sample was collected from the control plot at each sampling interval. Field fortifications were prepared after the fourth application on Days 1 (California and Louisiana), 2 (Texas), 4 (Louisiana and Texas), 5 (California), 13 (Louisiana), and 14 (California and Texas). Field fortification samples were produced using control plot leaf punch samples and were prepared at three fortification levels (~0.02, 1.0, and 10 $\mu g/cm^2$).

At each of the test sites, the maximum average corrected methyl parathion dislodgeable foliar residue (DFR) occurred immediately after the fourth application (2.12, 3.24, and 3.17 $\mu g/cm^2$ in California, Louisiana, and Texas respectively). The maximum average corrected methyl paraoxon DFR occurred 8-12 hours after the fourth application (0.0387, 0.0465, 0.0615 $\mu g/cm^2$ in California, Louisiana, and Texas respectively). The maximum average uncorrected 4-nitrophenol residue occurred on the day prior to the second application in Texas and Louisiana (0.0151 and 0.0137 $\mu g/cm^2$ respectively) while all values were <LOQ in California. The average corrected methyl parathion DFR declined to <LOQ (0.01 $\mu g/cm^2$) at the following times after the fourth application: at Day 14 (California), Day 7 (Louisiana and Texas). The average corrected methyl paraoxon DFR declined to <LOQ after the fourth application at Day 7 (California), Day 2 (Louisiana), and Day 3 (Texas).

The study author averaged corrected triplicate DFR values for methyl parathion and methyl paraoxon at each sampling interval from each test site. A separate dissipation model was generated for each analyte at each field site beginning with the samples collected immediately

after the fourth application through the first postapplication day where values were below LOQ. Values below LOQ were changed to ½ LOQ for use in the regression analysis. Microsoft's® Excel 2000 linear regression function was applied to the log (ln) transformed data. The study author's calculated dissipation half-lives and R^2 values were as follows:

- California - Methyl Parathion - 1.6 days (R^2=0.98)
- California - Methyl Paraoxon - 2.3 days (R^2=0.96)
- Louisiana - Methyl Parathion - 0.7 days (R^2=0.93)
- Louisiana - Methyl Paraoxon - 0.5 days (R^2=1.00)
- Texas - Methyl Parathion - 0.8 days (R^2=0.99)
- Texas - Methyl Paraoxon - 0.7 days (R^2=0.94)

The study author states that "the differences in humidity between the Louisiana and Texas sites (humid) and California (arid) site could be an explanation for the two-fold increase in methyl parathion half-life and the four-fold increase in methyl paraoxon half-life at the California site".

Versar used individual DFR values, not averages, in conducting linear regressions on the three data sets. Versar's calculated dissipation half-lives and R^2 values were as follows:

- California - Methyl Parathion - 1.4 days (R^2=0.96)
- California - Methyl Paraoxon - 3.0 days (R^2=0.89)
- Louisiana - Methyl Parathion - 0.5 days (R^2=0.95)
- Louisiana - Methyl Paraoxon - 0.5 days (R^2=0.86)
- Texas - Methyl Parathion - 0.7 days (R^2=0.82)
- Texas - Methyl Paraoxon - 1.1 days (R^2=0.80)

Since methyl parathion and methyl paraoxon are assumed to have the same toxicity, the their DFR values were averaged and then added together before running a regression analysis. Half of the LOQ value was used for the first LOQ value found in a series of LOQ values. The calculated dissipation half-lives and R^2 values were as follows for the combined residues:

- California - 1.6 days (R^2=0.98)
- Louisiana - 0.72 days (R^2=0.93)
- Texas - 0.76 days (R^2=0.99)

The study was in compliance with the major technical aspects of OPPTS Series 875 guidelines. There were issues and limitations of the data identified below.

- At the California site, one application of an herbicide was made just before the study period and two applications of insecticides were made during the study period. At the Louisiana site, two applications of fungicides, three applications of a plant growth regulator, one application of an insecticide (an organophosphate), and

two applications of herbicides were applied just before the study period and two applications of herbicides were applied during the study period. At the Texas site, one application of an insecticide (an organophosphate) and two applications of herbicides were made just before the study period. Five applications of insecticides (including 2 applications of an organophosphate insecticide), two applications of herbicides, and two applications of a bioregulator were applied during the study period. According to the protocol deviation documentation of August 16, 2000, no request was made for approval of these maintenance chemicals

STUDY REVIEW

Study Background

This report reviews a dislodgeable foliar residue (DFR) study in cotton plants submitted by Elf Atochem North America, Inc. in support of the reregistration of methyl parathion. The purpose of the study was to determine the residue levels of methyl parathion (O,O-Dimethyl O-p-nitrophenyl phosphorothioate - CAS No. 298-00-0, EPA Reg. No. 4581-393), and two metabolites/degradation products, methyl paraoxon (CAS No. 950-35-6) and 4-nitrophenol (CAS No. 100-02-7) that could be dislodged from cotton foliage after four ground spray applications of PENNCAP-M® Microencapsulated Insecticide at an application rate of 1.0 pounds ai per acre. PENNCAP-M® is a flowable formulation insecticide consisting of a water suspension of polymeric-type microcapsules, containing approximately 20.9 percent methyl parathion as the active ingredient (ai). PENNCAP-M® is labeled for use to control various foliar pests on corn, rice, soybeans, pecans, wheat, oats, barley, vegetable crops, and cotton. In cotton, the product is used to control flea hoppers, plant bugs, thrips, boll weevils, stink bugs, boll worms, white flies, lygus bugs, aphids, and soybean loopers.

The field portion of the study was performed at three field testing facilities (California, Texas, and Louisiana). All field and analytical operations were overseen by American Agricultural Services, Inc. of Cary, North Carolina. On-site field operations were conducted by Research for Hire, Inc. of Porterville, California, R&D Research, Inc. of Washington, Louisiana, and South Texas Ag Research of Uvalde, Texas. All DFR leaf samples were analyzed by Morse Laboratories, Inc. of Sacramento, California.

Cotton leaf punch samples were collected from treated and control plots in Porterville, California (June 5-August 2, 2000), Washington, Louisiana (May 11-July 8, 2000), and Uvalde, Texas (May 6-July 3, 2000). The sampling was performed the day prior to and the day following the first three applications, prior to the fourth application, immediately after the fourth application, 8-12 hours after the fourth application, Days 1,2,3,4 (Texas and Louisiana) or Day 5 (California), Days 7,10,13,14 (California and Texas sites), 21,28,35, and 42 days after the fourth application. A Birkestrand leaf punch sampler with a 1.0 inch punch diameter was used to

collect 40 leaf discs per sample. At each field test site, leaf punch samples were collected from three subplots in the treated plot. A single leaf punch sample was collected from the control plot at each sampling interval. Field fortifications were prepared after the fourth application on Days 1 (California and Louisiana), 2 (Texas), 4 (Louisiana and Texas), 5 (California), 13 (Louisiana), and 14 (California and Texas). Field fortification samples were produced using control plot leaf punch samples and were prepared at three fortification levels (~0.02, 1.0, and 10 $\mu g/cm^2$).

Test Plots

The test sites were located in major cotton growing regions of Porterville, California (representing EPA Region X), Washington, Louisiana (representing EPA Region IV), and Uvalde, Texas (representing EPA Region VI). The sites were used concurrently for a cotton scouting worker re-entry exposure study (KP-2000-02), as well as this DFR study. (Only the DFR studies are discussed in this review). According to the authors, the cotton was maintained in a healthy state for the duration of the study by standard agricultural practices and essential maintenance chemical applications. Cotton varieties used were *Delta Pine 6102* at the California site, *Suregrow 821* at the Louisiana site, and *SureGrow 125* at the Texas site. The test cotton was planted on May 4, 2000, March 23, 2000, and March 30, 2000 at the California, Louisiana, and Texas sites, respectively. Soil type at each site were loamy fine sand (California), silty clay loam (Louisiana), and clay loam (Texas). A treated and an untreated (control) plot were established at each test site.

The test site in California consisted of a treated plot measuring 19 x 180 feet. The treated plot was divided into three subplots (19 x 60 feet) to allow for triplicate sampling. The test site in Louisiana consisted a treated plot measuring 198 x 100 feet divided into three subplots (66 x 100 feet) for sampling, and the treated plot at the Texas site measured 26.67 x 200 ft and was divided into three subplots. Sample plot diagrams are provided on pages 82-84 of the study report.

Field and Pesticide Use History

Pesticide use for the field trial period for each of the sites was provided on page 55 of the study report. At the California site, one application of an herbicide was made just before the study period and two applications of insecticides were made during the study period. At the Louisiana site, two applications of fungicides, three applications of a plant growth regulator, one application of an insecticide (an organophosphate), and two applications of herbicides were applied just before the study period and two applications of herbicides were applied during the study period. At the Texas site, one application of an insecticide (an organophosphate) and two applications of herbicides were made just before the study period. Five applications of insecticides (including 2 applications of an organophosphate insecticide), two applications of herbicides, and two applications of a bioregulator were applied during the study period.

According to the protocol deviation documentation of August 16, 2000, no request was made for approval of these maintenance chemicals

No information was provided in the study report regarding field use history prior to the cotton plantings in 2000.

Materials and Applications

A product label for PENNCAP-M® (EPA Reg. No. 4581-393) was provided in the study report. PENNCAP-M® is a flowable formulation insecticide consisting of a water suspension of polymeric-type microcapsules which contain 2 pounds ai/gallon. The maximum label use rate for cotton is 1 pound ai per acre (i.e., 4 pints formulated product per acre). For this study, four ground spray applications of PENNCAP-M® were made at five day intervals using the maximum application rate of 1 pound ai per acre per application. The product label specifies that applications may be repeated as necessary to maintain control and did not specify either a minimum time interval between applications or a maximum number of applications per season. According to label instructions, PENNCAP-M® should not be applied if rainfall is expected within 6 hours of application.

At all field sites, the pesticide applications were made using a tractor mounted ground boom sprayer with hollow-cone or flat fan nozzles. Applications were made using 15.72-17.82 gallons per acre at the California site, 10.09-11.27 gallons per acre at the Louisiana site, and 10.55-10.74 gallons per acre at the Texas site. Equipment specifications were provided on pages 56 of the study report. Equipment was calibrated prior to each application.

Meteorology

The authors stated that: "maximum and minimum air temperature and rainfall data were collected from instruments located at the test sites and/or institutional, permanent weather recording stations (NOAA and others)". However, the location and distance of the nearest NOAA or other recording weather station was not recorded in the study report. Average monthly minimum and maximum temperature and precipitation data for the study months were reported, along with historical monthly (average) weather data (page 61 of the study report). The actual years and number of years used to determine historical average data was not specified.

On-site environmental data, such as wind speed, wind direction, air temperature, relative humidity, soil temperature, and soil moisture, were reported for the day of each application (page 59 of the study report). The PENNCAP-M® Microencapsulated Insecticide label states that rainfall soon after application may decrease effectiveness of PENNCAP-M®. The label further recommends that PENNCAP-M® should not be applied if rainfall is expected within 6 hours of application.

At the California test site, overall weather conditions were consistent with "historical" climatological data. No rainfall occured on any of the application days. There was also no rainfall during the sampling period after the fourth application. Air temperatures during the months of June, July and August ranged from 60°F to 98°F. At the Louisiana test site, the average high and low temperatures during the study (range of 60°F to 98°F) closely approximated the "historical" temperatures. There was significantly less rainfall during May and June (2.3 and 4.6 inches, respectively) than the "historical" levels (5.39 and 7.07 inches, respectively). No rainfall occured on any of the application days. There was 5.28 inches of rain during the sampling period after the fourth application, with the first rainfall event occuring 8 days after the fourth application (0.21 inches) and the highest daily rainfall event being 1.07 inches. At the Texas test site, weather conditions for May and June were consistent with "historical" data, while July was drier (0.06 inches of rainfall) than "historical" data (2.21 inches) and maximum air temperatures were higher (101.7°F) than "historical" air temperatures (97.6°F). On the day of the second application, 0.78 inches of rainfall occured. There was 6.66 inches of rain during the sampling period after the fourth application, with the first rainfall event occuring 5 days after the fourth application (1.16 inches) and the highest daily rainfall event being 1.83 inches. The study report states that no overhead irrigation was used after the test applications and sampling began. However, it is not known if furrow irrigation was used to maintain the health of the cotton crop.

Sampling of Leaf Dislodgeable Residue Samples

Leaf punch samples were collected at the following intervals: prior to each application, and the day following each application, just after the fourth application (after the spray had dried), 8-12 hours after the fourth application, and 1, 2, 3, 4 7, 10, 14, 21, 28, 35 and 42 days after the fourth application. At the California site, samples were collected on Day 5 instead of Day 4. At the Louisiana site, samples were collected on Day 13 instead of Day 14. At each interval, three replicate samples were collected from the treated plot (one from each of the three treated sub-plots) and one sample from the control plot. Control samples were also taken for the field fortification experiments after the fourth application at Day 1 (California and Louisiana), Day 2 (Texas), Day 4 (Louisiana and Texas), Day 5 (California), Day 13 (Louisiana), and Day 14 (California and Texas). All leaf punches were collected using a 1.0 inch diameter Birkestrand leaf punch sampler. Each sample consisted of four punches per plant taken randomly from ten plants to equal 40 punches for a total of 405 cm^2 leaf surface area, representing both sides of the leaf surface. Information on the sampling approach utilized was not provided in the report.

QA/QC

Sample Handling & Storage

At the field test site, leaf punch samples were dislodged twice with 100 mL of a 0.01%v/v aqueous solution of the wetting agent Aerosol® OT 75 [dioctyl sodium sulfosuccinate]. The authors noted that: "dislodging generally began within four hours of sampling." After

dislodging, leaf discs were discarded and the dislodging solution samples were immediately placed into freezer storage until shipment to the analytical laboratory.

Leaf punch extracts (including field fortified samples) were stored in freezers until shipment to the analytical laboratory. Samples were shipped to Morse Laboratories, Inc., in Sacramento, California via FedEx on dry ice, hand-delivery (California only) or via ACDS freezer truck service. All samples were identified with a unique sample number containing the study number, site identifier and a serial number. All samples were stored frozen prior to analysis. At Morse Laboratories, Inc., all samples were transferred to a limited-access freezer for storage. Freezer storage temperatures were monitored on a daily basis and were maintained at -20±5 °C. The maximum storage interval for any sample (from sampling to analysis) was approximately 75 days. Samples were analyzed between 7 and 10 weeks after collection. Table 1 of the study report (pages 128-135) summarizes the sampling-to-analysis interval data.

Tank Mix and Product Analyses

Information on tank mix analysis was not provided in the study report. The certified ai content of Penncap-M® was 21.1 percent (December 29, 1999).

Analytical Methodology

Morse Laboratories, Inc. analyzed samples of the Aerosol® OT-75 dislodging solution used to surface extract cotton foliage in order to determine dislodgeable residues of methyl parathion and methyl paraoxon. Some of the samples were also analyzed for 4-nitrophenol. In addition, field fortification samples, as well as in-lab storage stability samples, were analyzed.

The analytical method used for the analysis of methyl parathion and methyl paraoxon in DFR solutions was Morse Laboratories, Inc. Analytical Method No. 121, Revision #3, dated May 12, 2000, entitled "Determination of Methyl Parathion and its Oxygen Analog in Dislodgeable Foliar Residue (DFR) Solutions". A copy of the method was provided in Appendix I of the study report (page 208). THF (tetrahydrofuran) was added to a specific volume of dislodging solution to 1) dissolve the encapsulating material of the formulation, thereby releasing the methyl parathion (and any methyl paraoxon) and 2) provide a partition medium for subsequent extraction of the analytes from the aqueous sample. An excess of solid NaCl was added to totally saturate the aqueous component of the mixture, forcing the two solvents to separate. An aliquot of the organic phase was removed and purified by means of carbon black solid phase extraction (SPE) tube cleanup. The purified extract was concentrated and analyzed using gas chromatography employing flame photometric detection in the phosphorous mode. Calibration curves were generated by injecting constant volumes of mixed standard solutions. Sample responses greater than those produced by the highest concentration of applicable standard curve required dilution and reinjection. A curve check standard was injected every 4-5 sample injections. Sample chromatograms were included and showed good peak separation and

sharpness of peaks. Details of the instrument parameters were reported in Appendix B (Analytical Phase Report) of the study report (page 110).

The analytical method used for the analysis of 4-nitrophenol (a degradation product of several organophosphate insecticides including methyl parathion) in DFR solutions was Morse Laboratories, Inc. Analytical Method No. 126, Revision #3, entitled "Determination of 4-Nitrophenol in Dislodgeable Foliar Residue (DFR) Solutions." A copy of the method was provided in Appendix II of the study report (page 230). 4-Nitrophenol was isolated from the DFR dislodging solutions by extraction with toluene. MTBSTFA [N-(tert-Butyldimethylsilyl)-N-methyltrifluoroacetamide] was added to a diluted form of the toluene extract which converted any 4-nitrophenol present to the more volatile tert-butyldimethylsilyl derivative. All samples were analyzed using a gas chromatograph equipped with a mass selective detector. Representative chromatograms of standards and fortified samples are provided in the study report. Chromatograms show good peak separation and sharpness of peaks.

Limits of Detection (LOD) & Limit of Quantitation (LOQ) / Control Samples

The limit of detection (LOD) for methyl parathion, methyl paraoxon, and 4-nitrophenol was 0.003 $\mu g/cm^2$ and the limit of quantitation (LOQ) was 0.01 $\mu g/cm^2$. Untreated control samples detected no residues of either methyl parathion, methyl paraoxon, or 4-nitrophenol above the LOQ.

Laboratory Recovery

To evaluate the performance of the analytical method, laboratory fortification samples were analyzed concurrently with each set of samples by fortifying a control sample with an appropriate amount of the fortification standard. Each sample set of laboratory recovery samples contained one laboratory control and two laboratory fortifications. The overall average recovery was 86 percent ± 6 (n=62) for methyl parathion (ranging from 70 to 100 percent), 93 percent ± 8.5 (n=62) for methyl paraoxon (ranging from 69 to 120 percent), and 87 percent ± 7.9 (n=8) for 4-nitrophenol (ranging from 73 to 96 percent). Individual recovery values are provided in Tables 4 and 5 of the study report (pages 146-149).

Field Fortification Recovery

Field-fortified samples were prepared at three fortification levels for methyl parathion and methyl paraoxon analysis. No field fortifications were conducted using 4-nitrophenol. Samples were fortified at 0.02, 1.0, and 10 $\mu g/cm^2$, representing 2X, 100X, and 1,000X the LOQ, respectively. Control leaf punches were collected for field fortification on Days 1 (Louisiana and California), 2 (Texas), 4 (Louisiana and Texas), 5 (California), 13 (Louisiana), and 14 (California and Texas) after the fourth application. Dislodging solutions used for spiking were produced by collecting and rinsing control plot leaf punch samples. The dislodged extracts were spiked, stored frozen and treated under the same conditions as the DFR samples collected at the same

intervals. Table 1 summarizes the overall average corrected field fortified sample recovery results.

Table 1. Summary of Average Field Fortification Recoveries*

Test Substance		Texas	Louisiana	California
Methyl Parathion	Mean:	99%	104%	102%
	Standard Deviation:	±5.2	±18	±6.0
	Range (n=9) :	93% to 109%	72% to 139%	94% to 109%
Methyl Paraoxon	Mean:	93%	101%	91%
	Standard Deviation:	±11	±12	±8.5
	Range (n=9):	81% to 110%	82% to 118%	76% to 103%

* Corrected for average procedural (laboratory) recovery within the analytical set.

Corrected recoveries for methyl parathion averaged 102 percent, 104 percent, and 99 percent at the California, Louisiana, and Texas sites, respectively. Corrected recoveries for methyl paraoxon averaged 91 percent, 101 percent, and 93 percent at the California, Louisiana, and Texas sites, respectively. Tables 7a, 7b, and 7c (Pages 151-153) of the study report identify individual recovery values.

Storage Stability Recovery

Frozen storage stability for methyl parathion and methyl paraoxon in DFR solutions was determined during performance of a study of PENNCAP-M® application to sweet corn (MRID # 452697-01 and 452889-01). Stability results demonstrate stability for frozen storage periods of up to 168 days. This supports the 74 day storage period pertinent to this study.

Results

Average DFR data for methyl parathion and methyl paraoxon are summarized in Table 2. Average 4-nitrophenol residues found for selected sampling sites are summarized in Table 3. The DFR values were corrected using the overall average field fortification recoveries for methyl parathion and methyl paraoxon when overall average field fortified recovery values from the respective field sites were <100 percent. The following data were corrected: Methyl paraoxon values from California (91 percent field fortification recovery), methyl parathion and paraoxon values from Texas (99 and 93 percent field fortification recovery). No residues above LOQ of methyl parathion, methyl paraoxon, or 4-nitrophenol were found in any untreated control samples.

At each of the test sites, the maximum average corrected methyl parathion dislodgeable foliar residue (DFR) occurred immediately after the fourth application (2.12, 3.24, and 3.17 $\mu g/cm^2$ in

California, Louisiana, and Texas respectively). The maximum average corrected methyl paraoxon DFR occurred 8-12 hours after the fourth application (0.0387, 0.0465, 0.0615 $\mu g/cm^2$ in California, Louisiana, and Texas respectively). The maximum average uncorrected 4-nitrophenol residue occurred on the day prior to the second application in Texas and Louisiana (0.0151 and 0.0137 $\mu g/cm^2$ respectively) while all values were <LOQ in California. The average corrected methyl parathion DFR declined to <LOQ (0.01 $\mu g/cm^2$) at the following times after the fourth application: at Day 14 for the California site, Day 7 for the Louisiana and Texas sites. The average corrected methyl paraoxon DFR declined to <LOQ after the fourth application at Day 7 for the California site, Day 2 for the Louisiana site, and Day 3 for the Texas site.

Regression Calculations

Calculation of methyl parathion and methyl paraoxon residue levels were conducted using a validated software application to create a standard curve based on linear regression. A standard curve based on non-linear regression was used to calculate 4-nitrophenol residue levels. Adjustments in the raw data for methyl parathion and methyl paraoxon were made for the overall average field fortification recoveries. No adjustments in the raw data were made for 4-nitrophenol and no further analyses of these data were conducted. Statistical analysis of the residue data was limited to arithmetic mean, standard deviation, and regression analysis.

The study author averaged corrected triplicate DFR values for methyl parathion and methyl paraoxon at each sampling interval from each test site . First-order kinetics was used to predict the residue half-life. A separate dissipation model was generated for each analyte at each field site beginning with the samples collected immediately after the fourth application through the first postapplication day where values were below LOQ for methyl parathion. For methyl paraoxon the dissipation was calculated using data beginning with the 8-12 hour samples through the first postapplication day where values were below LOQ. Microsoft's® Excel 2000 linear regression function was applied to the log (ln) transformed data. As shown in Tables 4a and 4b, regression analysis of the methyl parathion residue data indicates that the dissipation half-life was 1.6 days in California, 0.7 days in Louisiana, and 0.8 days in Texas. Methyl paraoxon half-lives were 2.3 days (California), 0.5 days (Louisiana) and 0.7 days (Texas). The study author states that "the differences in humidity between the Louisiana and Texas sites (humid) and California (arid) site could be an explanation for the two-fold increase in methyl parathion half-life and the four-fold increase in methyl paraoxon half-life at the California site.

A regression analysis was done for both methyl parathion and methyl paraoxon. Versar used individual data points, not averages, in conducting linear regressions of the data. Like the regressions submitted by the registrant, Versar corrected the field data using the overall corrected average field fortification recovery values for those test sites and analytes when corrected field fortifications were less than 100 percent (i.e., methyl parathion in Texas (field recovery 99 percent), methyl paraoxon in Texas (field fortification recovery = 93 percent), and methyl paraoxon in California (field fortification recovery = 91 percent)). In the Versar analysis, only DFR values above LOQ were included in the regression analysis except in the one instance

where only 2 data sets had DFR levels >LOQ (i.e., methyl paraoxon in Louisiana). To predict dissipation for this location, application #2, 0 hours after application data (where all replicates had values <LOQ) were used in the regression analysis (see Appendix A). See Tables 4a and 4b for a comparison of Versar's and the study author's calculated half lives for methyl parathion and methyl paraoxon.

A regression analysis was also done for methyl parathion and methyl paraoxon together. Since no toxicity data exists for methyl paraoxon, it is assumed to have similar toxicity to methyl parathion. Therefore, exposures to both methyl parathion and methyl paraoxon should be assessed together. The was done by averaging the three replicates for both methyl parathion and methyl paraoxon, then adding averages together for each sampling period.. Like the regressions submitted by the registrant, the field data was corrected, using the overall corrected average field fortification recovery values, for the data from test sites where field fortifications were less than 100 percent for either methyl parathion or methyl paraoxon (i.e., methyl parathion in Texas (field recovery 99 percent), methyl paraoxon in Texas (field fortification recovery = 93 percent), and methyl paraoxon in California (field fortification recovery = 91 percent)). In the analysis, for DFR values less than the LOQ (0.01 $\mu g/cm^2$), half of the LOQ value was used for the first value less than the LOQ in a series of DFR values less than the LOQ.

Table 2. Summary of Average DFR Residue Data by Sampling Interval (corrected when overall field recovery <100% for the respective test site)

Sampling Interval (time after specified application)	California			Louisiana			Texas		
	Methyl Parathion ($\mu g/cm^2$) not corrected	Methyl Paraoxon ($\mu g/cm^2$) corrected	Methyl Parathion and Methyl Paraoxon ($\mu g/cm^2$)	Methyl Parathion ($\mu g/cm^2$) not corrected	Methyl Paraoxon ($\mu g/cm^2$) not corrected	Methyl Parathion and Methyl Paraoxon ($\mu g/cm^2$)	Methyl Parathion ($\mu g/cm^2$) corrected	Methyl Paraoxon ($\mu g/cm^2$) corrected	Methyl Parathion and Methyl Paraoxon ($\mu g/cm^2$)
Pre-Application	<0.01	<0.01	-	<0.01	<0.01	-	<0.01	<0.01	-
App #1 Hour 0	0.2390	0.0133	0.2523	0.6850	0.0180	0.7030	0.7273	0.0235	0.7508
App #2 Hour 0	0.3420	0.0159	0.3579	0.8550	0.0301	0.8851	1.6970	0.0540	1.7510
App #3 Hour 0	0.4120	0.0191	0.4311	0.5240	0.0137	0.5377	1.2828	0.0323	1.3151
App #4 Hour 0	2.12	<0.01	2.1250	3.2400	0.0379	3.2779	3.1717	0.0423	3.2140
App #4 Hour 8-12	1.15	0.0387	1.1890	1.5600	0.0465	1.6065	1.9293	0.0615	1.9908
App #4 Day 1	1.03	0.0375	1.0675	0.8460	0.0251	0.8711	1.1313	0.0463	1.1776
App #4 Day 2	0.4220	0.0290	0.4510	0.1840	<0.01	0.1850	0.3949	0.0249	0.4198
App #4 Day 3	0.3430	0.0248	0.3678	0.0482	<0.01	0.0482	0.1374	<0.01	0.1424
App #4 Day 4	N/S	N/S	N/S	0.0164	<0.01	0.0164	0.0994	<0.01	0.0994
App #4 Day 5	0.1800	0.0137	0.1937	N/S	N/S	N/S	N/S	N/S	N/S
App #4 Day 7	0.0800	<0.01	0.085	<0.01	<0.01	0.005	<0.01	<0.01	0.005
App #4 Day 10	0.0102	<0.01	0.0102	<0.01	<0.01	-	<0.01	<0.01	-
App #4 Day 13	N/S	N/S	N/S	<0.01	<0.01	-	N/S	N/S	N/S
App #4 Day 14	<0.01	<0.01	0.005	NA	NA	NA	<0.01	<0.01	-
App #4 Day 21	<0.01	<0.01	-	NA	NA	NA	NA	NA	NA
App #4 Day 28	<0.01	<0.01	-	NA	NA	NA	NA	NA	NA

- NA = Not analyzed N/S = Not sampled

Table 3. Average 4-nitrophenol DFR Residues Found at Selected Sampling Events.

Sampling Events	California site ($\mu g/cm^2$)	Louisiana site ($\mu g/cm^2$)	Texas site ($\mu g/cm^2$)
Application 1, Day 1	NA	< 0.01	< 0.01
Application 2, Day 1	NA	0.0137	0.0151
Application 3, Day 1	NA	< 0.01	0.0105
Application 4, Day 4	NA	< 0.01	< 0.01
Application 4, Day 5	< 0.01	NA	NA

Table 4a. Methyl Parathion Half-lives as Estimated by Elf Atochem North America and Versar

Data Used for Regression	California		Louisiana		Texas	
	Half-life (days)	R^2	Half-life (days)	R^2	Half-life (days)	R^2
Elf Atochem North America[a]	1.6	0.98	0.7	0.93	0.8	0.99
Versar[b]	1.4	0.96	0.5	0.95	0.7	0.82

[a] Regression data: 0 to 14 days after the fourth application at the California site, and 0 to 7 days after the fourth application at the Louisiana and Texas test sites. DFR values corrected using average field fortification recovery values. Values <LOQ reported as ½ LOQ for purpose of regression analysis.

[b] Regression data: 0 to 7 days after the fourth application at the California site, and 0 to 4 days after the fourth application at the Louisiana test sites and 0 to 4 days after the fourth application for the Texas site. DFR values corrected using average field fortification recovery values. Regression performed using data from those days where ≥2 of the replicates were > LOQ.

Table 4b. Methyl Paraoxon Half-lives as Estimated by Elf Atochem North America and Versar

Data Used for Regression	California		Louisiana		Texas	
	Half-life (days)	R^2	Half-life (days)	R^2	Half-life (days)	R^2
Elf Atochem North America[a]	2.3	0.97	0.5	1.0	0.7	0.94
Versar[b]	3.0	0.89	0.5	0.86	1.1	0.80

[a] Regression data: 8-12 hours after application to the seventh day after the fourth application at the California site, and 8-12 hours after application to 2 days after the fourth application at the Louisiana test site and 8-12 hours after application to 3 days after the fourth application at the Texas test site. DFR values corrected using average field fortification recovery values. Values <LOQ reported as ½ LOQ for purpose of regression analysis.

[b] Regression data: 8-12 hours after fourth application to 5 days after the fourth application at the California site, and 8-12 hours after fourth application through 2 days after the fourth application at the Louisiana test sites and 8-12 hours after fourth application through 2 days after the fourth application for the Texas site. DFR values corrected using average field fortification recovery values. Regression perform using data from those days where ≥2 of the replicates were > LOQ.

For the combined methyl parathion and methyl paraoxon residue values, the calculated dissipation half-lives and R^2 values from the regression analysis were as follows:

- California - 1.6 days (R^2=0.98)
- Louisiana - 0.72 days (R^2=0.93)
- Texas - 0.76 days (R^2=0.99)

Compliance Checklist

Compliance with OPPTS Series 875, Occupational and Residential Exposure Test Guidelines, Group B: Postapplication Exposure Monitoring Test Guidelines, 875.2100, Foliar Dislodgeable Residue Dissipation: Agricultural, is critical. The itemized checklist below describes compliance with the major technical aspects of OPPTS 875.2100, and is based on the "Checklist for Residue Dissipation Data":

- *Typical end use product of the active ingredient used.* This criterion was met.

- *Dislodgeable foliar residue (DFR) data should be collected from at least three geographically distinct locations for each formulation.* This criterion was met. DFR data were collected in Texas, California and Louisiana representing three different EPA regions. These geographic sites were appropriate testing locations as Texas and California ranked one and two in cotton production in 1997 accounting for approximately 41 percent of the total U.S. cotton production. Louisiana ranked sixth (5 percent).

- *The production of metabolites, breakdown products, or the presence of contaminants of concern, should be considered in the study design on a case-by-case basis.* This criterion was met. Residues from methyl paraoxon, an oxygen analog of methyl parathion, and 4-nitrophenol, a degradation product, were also analyzed.

- *Site(s) treated should be representative of reasonable worst-case climatic conditions expected in intended use areas.* This criterion was met. Whether or not reasonable "worst-case" climatic conditions were captured is unknown. The climatological data for the testing period in California and Texas indicated no significant departure from the "normal" air temperature and historical rainfall amounts during the trial period except in July which was significantly hotter and dryer than the historical conditions. The rainfall data for the testing period in Louisiana was significantly drier than "normal" conditions while temperatures were similar to historical air temperatures. The study report does not identify the dates or number of years chosen to represent historical conditions.

- *End use product applied by application method recommended for the crop. Application rate given and should be at the least dilution and highest, label permitted, application rate.* These criteria were met. Applications were made using the maximum label rate of 4 pints formulated product per acre or 1 pound ai per acre. The formulated product contains 2 pounds of active ingredient per gallon. The application volume ranged between 10 and 18 gallons/acre, and the label only recommended minimum dilution volume for

aerial application (2 gallons/acre) not ground application. [The Study Protocol specified an application volume of no more than 20 gallons/acre (±5 percent).]

- *Applications occurred at time of season that the end-use product is normally applied to achieve intended pest control.* This criterion was met. Applications were made in May (Texas and Louisiana) and in June (California). The fourth and final applications were made 4-5 days prior to worker-reentry as specified on the label.

- *If multiple applications are made, the minimum allowable interval between applications should be used.* This criterion was met. The product label states that applications may be repeated as necessary to maintain control of pests. Four applications, 5 days apart, were made at each test site.

- *Sampling should be sufficient to cover three half-lives and establish a dissipation curve. Recommended sampling intervals are 1 hour, 4 hours, 8 hours, 12 hours, 1, 2, and 3 days after application.* This criterion was met. Half-life values were 1.6 days, 0.7 days, and 0.8 days for methyl parathion in California, Louisiana, and Texas, respectively. Half-life values were 2.3 days, 0.5 days, and 0.7 days for methyl paraoxon in California, Louisiana, and Texas, respectively. DFR samples were collected at the following intervals: prior to each application, and the day following each application, just after the fourth application (after the spray had dried), 8-12 hours after the fourth application, and on Days 1, 2, 3, 4 7, 10, 14, 21, 28, 35 and 42 after the fourth application. At the California site, samples were collected on Day 5 instead of Day 4. At the Louisiana site, samples were collected on Day 13 instead of Day 14.

- *Meteorological conditions including temperature, wind speed, daily rainfall, and humidity should be provided for the duration of the study.* This criterion was met. Air temperature readings, relative humidity, wind speed and direction, cloud cover, and soil moisture and temperature are summarized in the study report for the days of application at each test site. Monthly air temperature and precipitation data are provided for the two months of application and sampling.

- *Residue storage stability, method efficiency (residue recovery), and limit of quantitation (LOQ) should be provided.* These criteria were met. Laboratory recovery (method efficiency) for methyl parathion averaged 86 percent ± 6 and fortified field recovery averaged 87.9 percent (n=27). The LOQ was reported as 0.01 $\mu g/cm^2$ for all three analytes. Storage stability study data are presented in an additional methyl parathion DFR study - *Amended Final Report Foliar Dislodgeable Residue Dissipation of PENNCAP-M® in Sweet Corn MRID # 452889-01.*

- *Triplicate, randomly collected samples should be collected at each sampling interval.* This criterion was met. Triplicate samples were collected at each sampling interval.

- *Control and baseline foliar or soil samples should collected.* The criterion was met. Control samples were collected from the control plot at each sampling interval. No soil samples were collected.

Other issues and limitations of the data are identified below:

- The leaf punch sampling approach was not thoroughly discussed.
- Information on tank mix analysis was not provided in the study report.
- At the California site, one application of an herbicide was made before the study period and two applications of insecticides were made during the study period. At the Louisiana site, two applications of fungicides, three applications of a plant growth regulator, one application of an insecticide (an organophosphate), and two applications of herbicides were applied before the study period and two applications of herbicides were applied during the study period. At the Texas site, one application of an insecticide (an organophosphate) and two applications of herbicides were made before the study period. Five applications of insecticides (including 2 applications of an organophosphate insecticide), two applications of herbicides, and two applications of a bioregulator were applied during the study period. According to the protocol deviation documentation of August 16, 2000, no request was made for approval of these maintenance chemicals.