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HEALTH EFFECTS DIVISION
SCIENTIFIC DATA REVIEWS
EPA SERIES 361

OFFICE OF PREVENTION, PESTICIDES AND TOXIC SUBSTANCES

July 31, 2001

Memorandum

SUBJECT: Review of *Postapplication Exposure Monitoring: Foliar Dislodgeable Residue Dissipation of PENNCAP-M® in Sweet Corn (EPA Region I)*
MRID No. 452750-01

FROM: Renee Sandvig, Environmental Protection Specialist Renee Sandvig 7/31/01
Reregistration Branch II
Health Effects Division (7509C)

THRU: Al Nielsen, Branch Senior Scientist Al Nielsen 7/31/01
Reregistration Branch II
Health Effects Division (7509C)

TO: Diana Locke, Ph.D.
Risk Assessor
Reregistration Branch II
Health Effects Division (7509C)

DP Barcode: D271209

Pesticide Chemical Codes: 053501

EPA MRID Numbers: 452750-01

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 20, 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 sweet corn 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

This report reviews a dislodgeable foliar residue (DFR) study submitted by Elf Atochem North America, Inc. in response to an August 2, 1999 Memorandum of Agreement between the U.S. Environmental Protection Agency (U.S. EPA) and Elf Atochem. The insecticide methyl parathion was applied to sweet corn in one geographical location in Lyons, New York (a companion sweet corn study was conducted at a earlier date in California and Florida). The insecticide was applied as PENNCAP-M®, a flowable formulation consisting of a water suspension of polymeric-type microcapsules containing 20.9 percent methyl parathion. This study was conducted to determine the residue levels of methyl parathion and one metabolite/degradation product, methyl paraoxon, that can be dislodged from sweet corn foliage following four ground spray applications of the test substance at a rate of 0.75 pounds active ingredient (ai) per acre per application.

The test site received approximately one inch less rainfall (2.62 inches) during the study than that reported by historical data during August (3.5 inches). September precipitation (3.75 inches) was approximately the same as historical data. Additional data were presented by the on-site computerized weather station at the time of each application: relative humidity was 80-95 percent, soil temperature at 2 inches was 46 to 80°F, and at 6 inches was 42 to 74°F, soil was reported as moist, wind speed and direction was 0-4 mph from the west, and cloud cover was reported as 0 to 100 percent. No overhead irrigation was applied during the treatment period. However, precipitation is reported to have occurred on each day of application (application 1-4) at 0.23, 0.03, 0.03, and 0.04 inches, respectively.

Sweet corn leaf punch samples were collected from two treated and one control plot in Lyons, New York (August 8 to September 22, 2000). Each treated plot (i.e., Treatment #2 and Treatment #3) received applications of a different batch number of PENNCAP-M®. Versar used individual corrected DFR values (non-filtered samples), not averages, in conducting linear regressions on the three data sets. Versar corrected all of the field data using the average field fortification recovery values for methyl parathion and methyl paraoxon from the respective test plot (Table 1). Only DFR values greater than the LOQ were included, with the exception of Treatment #3, DAT-28 and 35, where, for calculation purposes, the replicate with a value of less than the LOQ was given a value of ½ LOQ.

Versar's calculated dissipation half-lives and correlation coefficients were as follows:

- Methyl parathion (Treatment #2 plot)- 1.1 days ($R^2$=0.96)
- Methyl parathion (Treatment #3 plot)- 3.5 days ($R^2$=0.83)

Since methyl parathion and methyl paraoxon are assumed to have the same toxicity, their individual DFR replicate values for each sampling period 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. Half of the LOQ (0.01 $\mu g/cm^2$) was also added to the methyl parathion residue on the day of the fourth application since measurable levels of methyl paraoxon were found before and after this study period. An analysis of the combined residues was only done for treatment #2 plot, not treatment #3 plot, since no methyl paraoxon was found in any sampling interval at the treatment #3 plot. Regression analysis of the combined residue data from treatment #2 plot indicates that the dissipation half-life was 1.1 days, with an $R^2$ value of 0.97. This half life value is the same as the half life values calculated by Versar and the study author for methyl parathion at treatment #2 plot.

The study was in compliance with the major technical aspects of OPPTS Series 875 guidelines. The most important issues of concern are identified below:

- The product was not applied at the maximum rate. The label states that the maximum application rate for sweet corn is 4 pints of formulated product per acre (1.0 pound ai per acre). In this study, sweet corn grown in New York were sprayed four times at the rate of 3 pints per acre (0.75 pounds ai per acre). The EPA review, dated February 22, 2000, of the initial study protocol submitted by the registrant states that the study must be conducted at the maximum application rate for the crop used and that 1 lb ai/acre is the application rate that should be used in this study.

- Rainfall is reported to have occurred each day of application, 0.23, 0.03, 0.03, and 0.04 inches.

- 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: Al Nielsen
Margarita Collantes
1000.001-01 file

**FROM:** Eric Grape/Susan Anderson

**DATE:** February 20, 2001

**SUBJECT:** Review of Foliar Dislodgeable Residue Study: *Postapplication Exposure Monitoring: Foliar Dislodgeable Residue Dissipation of PENNCAP-M® in Sweet Corn (EPA Region I)* MRID No. 452750-01

This report reviews the foliar dislodgeable residue study: *Postapplication Exposure Monitoring: Foliar Dislodgeable Residue Dissipation of PENNCAP-M® in Sweet Corn (EPA Region I)*, submitted by Cerexagri, Inc. (formerly Elf Atochem North America, Inc.) in response to an August 2, 1999 Memorandum of Agreement between the U.S. Environmental Protection Agency (U.S. EPA) and Elf Atochem. A summary of the study and its compliance with the U.S. EPA's Office of Pollution Prevention and Toxics (OPPTS) Series 875, Occupational and Residential Exposure Test Guidelines, Group B: Postapplication Exposure Monitoring Test Guidelines, 875.2100, Dislodgeable Foliar Residue Dissipation is provided. The following information may be used to identify the study:

| | |
|---|---|
| Study Title: | *Postapplication Exposure Monitoring: Foliar Dislodgeable Residue Dissipation of PENNCAP-M® in Sweet Corn (EPA Region I); 285 pages* |
| Sponsor/Representative: | Elf Atochem North America, Inc.<br>Agrichemicals Division<br>2000 Market Street, 21st Floor<br>Philadelphia, PA 19103-3222<br><br>Rodney Bennett<br>Elf Atochem North America, Inc.<br>900 First Avenue<br>King of Prussia, PA 19406 |
| Field Study Test Sites: | A.C.D.S. Research, Inc.<br>9813 Glenmark Road<br>North Rose, NY 14516 |
| Analytical Laboratory: | Frances Brookey, Principal Analytical Investigator<br>Morse Laboratories, Inc.<br>1525 Fulton Avenue<br>Sacramento, CA 95825 |
| Study Director and Author: | William P. Barney<br>Grayson Research, LLC.<br>1040 Grayson Farm Road<br>Creedmoor, NC 27522 |
| Report Date: | November 27, 2000 |
| Identifying Codes: | MRID # 452750-01; Study # KP-2000-08; Project # ML00-0864-ATO |

## EXECUTIVE SUMMARY

This report reviews a dislodgeable foliar residue (DFR) study submitted by Elf Atochem North America, Inc. in response to an August 2, 1999 Memorandum of Agreement between the U.S. Environmental Protection Agency (U.S. EPA) and Elf Atochem. The insecticide methyl parathion was applied to sweet corn in one geographical location in Lyons, New York (a companion sweet corn study was conducted at a earlier date in California and Florida). The insecticide was applied as PENNCAP-M®, a flowable formulation consisting of a water suspension of polymeric-type microcapsules containing 20.9 percent methyl parathion. This study was conducted to determine the residue levels of methyl parathion and one metabolite/degradation product, methyl paraoxon, that can be dislodged from sweet corn foliage following four ground spray applications of the test substance at a rate of 0.75 pounds active ingredient (ai) per acre per application.

Sweet corn leaf punch samples were collected from two treated and one control plot in Lyons, New York (August 8 to September 22, 2000). Each treated plot (i.e., Treatment #2 and Treatment #3) received applications of a different batch number of PENNCAP-M®. Sampling was performed prior to, and immediately after each of the four applications, and on DAT-0.3, 1, 2, 3, 4, 7, 14, 21, 28, and 35. A Birkestrand leaf punch sampler with a 2.523 cm punch diameter was used to collect 40 leaf discs per sample. Control and site samples were collected at each sampling interval. Field fortified samples were prepared after the first application and after the 24 hour sampling interval (DAT-1).

Methy parathion residues from both selected filtered and non-filtered sample analyses were presented in this study report. However, residue concentrations from the non-filtered sample analyses were consistently higher than the filtered analysis concentration results. Only the non-filtered analytical results are presented in this report.

The maximum average methyl parathion residue occurred immediately following the 3rd application at the Treatment #3 plot (2.05 $\mu g/cm^2$). Although methyl parathion residues decreased to less than an LOQ of 0.001 $\mu g/cm^2$ at DAT-21 at the Treatment #2 plot, detectable values at the Treatment #3 plot were detected on the last study sampling event on DAT-35.

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 methyl parathion at each of the two test plots beginning with the samples collected immediately after the fourth application through the first postapplication day where values were below the LOQ. Microsoft's® Excel 2000 linear regression function was applied to the log (ln) transformed data. Methyl paraoxon levels were below the LOQ following the final (4th) application and regression analyses were not performed.

The study author's calculated dissipation half-lives and correlation coefficients were as follows:

- Methyl parathion (Treatment #2 plot)- 1.1 days ($R^2$=0.97)
- Methyl parathion (Treatment #3 plot)- 3.7 days ($R^2$=0.84)

Versar used individual corrected DFR values (non-filtered samples), not averages, in conducting linear regressions on the three data sets. Versar corrected all of the field data using the average field fortification recovery values for methyl parathion and methyl paraoxon from the respective test plot (Table 1). Only DFR values greater than the LOQ were included, with the exception of Treatment #3, DAT-28 and 35, where, for calculation purposes, the replicate with a value of less than the LOQ was given a value of ½ LOQ.

Versar's calculated dissipation half-lives and correlation coefficients were as follows:

- Methyl parathion (Treatment #2 plot)- 1.1 days ($R^2$=0.96)
- Methyl parathion (Treatment #3 plot)- 3.5 days ($R^2$=0.83)

Since methyl parathion and methyl paraoxon are assumed to have the same toxicity, their individual DFR replicate values for each sampling period 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. Half of the LOQ (0.01 $\mu g/cm^2$) was also added to the methyl parathion residue on the day of the fourth application since measurable levels of methyl paraoxon were found before and after this study period. An analysis of the combined residues was only done for treatment #2 plot, not treatment #3 plot, since no methyl paraoxon was found in any sampling interval at the treatment #3 plot. Regression analysis of the combined residue data from treatment #2 plot indicates that the dissipation half-life was 1.1 days, with an $R^2$ value of 0.97. This half life value is the same as the half life values calculated by Versar and the study author for methyl parathion at treatment #2 plot.

The study was in compliance with most of the major technical aspects of Office of Pollution Prevention and Toxics (OPPTs) Series 875 guidelines. The most important issues of concern are identified below:

- The product was not applied at the maximum rate. The label states that the maximum application rate for sweet corn is 4 pints of formulated product per acre (1.0 pound ai per acre). In this study, sweet corn grown in New York were sprayed four times at the rate of 3 pints per acre or 0.75 pounds ai per acre. The EPA review, dated February 22, 2000, of the initial study protocol submitted by the registrant states that the study must be conducted at the maximum application rate for the crop used and that 1 lb ai/acre is the application rate that should be used in this study.

- Rainfall is reported to have occurred each day of application, 0.23, 0.03, 0.03, and 0.04 inches, and it is not possible to determine whether rainfall occurred within 24 hours of sample collection.

## STUDY REVIEW

### Study Background

This report reviews a dislodgeable foliar residue (DFR) study in sweet corn submitted by Elf Atochem North America, Inc. The study was conducted in response to an August 2, 1999 Memorandum of Agreement between U.S. EPA and Elf Atochem North America, Inc. Methyl parathion, CAS No. 298-00-0, is an organophosphate active ingredient (ai) in PENNCAP-M®, the insecticide formulation applied in this study. PENNCAP-M® is a flowable formulation consisting of a water suspension of polymeric-type microcapsules, which contain 20.9 percent methyl parathion. PENNCAP-M® is used to control insect pests in a variety of commercially important crops. In sweet corn, PENNCAP-M® is used to control corn rootworm adults, stinkbugs, aphids, flea beetles, grasshoppers, True army worms, European corn borers, Japanese beetles, sap beetles, silk fly, and black cutworms. The objective of this study was to determine the residue levels of methyl parathion and its metabolite/degradation product, methyl paraoxon (CAS No. 950-35-6), that can be dislodged from sweet corn foliage following four foliar applications of the test substance each at an application rate of 0.75 pounds ai per acre. Two different batches were used in this study.

The field portion of the study was conducted at one geographical location in Lyons, New York. A companion sweet corn DFR study (MRID No. 45269701) was conducted in California and Florida at an earlier date. All field and analytical operations were overseen by Grayson Research, LLC, of Creedmoor, North Carolina. On-site field operations were conducted by A.C.D.S. Research, Inc. of North Rose, New York. All DFR leaf samples were analyzed by Morse Laboratories, Inc. of Sacramento, California.

Leaf punch sampling was performed prior to and immediately after each of the four applications and at DAT-0.3, 1, 2, 3, 4, 7, 10, 14, 21, 28, and 35 after the last application. Ground spray applications of the test substance were made between August 9 and August 18, 2000. Samples were collected between August 8 and September 22, 2000. All dislodgeable samples were stored frozen for a period ranging from 1 to 77 days before extraction and analysis.

### Test Plots

The field test site was located in a major sweet corn production area in Lyons, New York (representing EPA Region I). Three plots were established at the test site. One plot was designated as the untreated control plot and two plots were designated as treated plots (one plot for each of two batches of PENNCAP-M®). The sweet corn was planted and cultured using

normal agronomic practices for sweet corn production. The planting date was Spring 2000. The sweet corn variety was *Rogers GH2783*. The soil type was Oakville sand.

Each of the two treated plots (Treatment 2 and 3) of the test site encompassed an area of 3,600 $ft^2$ (36 x 100 feet) comprised of 12 rows, each 3 x 100 feet. The treated plots were divided into three subplots to allow for triplicate sampling. The untreated control plot (Treatment 1) encompassed an area of 600 $ft^2$ (6 x 100 feet) comprised of 2 rows, each 3 x 100 feet. The control plot was established approximately 483 feet west of the nearest treated plot (Treatment 2). The treated plots were separated by 205 feet. Sample plot diagrams are provided on pages 69 of the study report.

**Field and Pesticide Use History**

Plot history indicates that a variety of crops were grown in rotation since 1997-1999, namely alfalfa/clover, bluegrass, turf, tomato, spinach, and tart cherry. The most recent crop grown in the treated plots were tart cherry (1999), and tomato (1999) in the control plot.

Maintenance chemicals were applied in late May 2000 just before the study period, and included 15-15-15 fertilizer (260 pounds/acre), Prowl 3.3 EC (1.5 pounds ai/acre), Dual Magnum 7.62 EC (1.27 pounds ai/acres), and Atrazine (1.5 pounds ai/acre). Historical test plot chemical use data (1997 - 1999) are provided on page 57 of the study report.

**Materials and Application**

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. It can be applied using air or ground equipment by diluting it with an amount of water suitable for the specific corp and type of spraying equipment. The maximum application rate for sweet corn is 4 pints of formulated product per acre or 1.0 pound ai/acre. Applications may be repeated as necessary to maintain control. The product label did not specify either a minimum time interval between applications or a maximum number of applications per season. The label states that rainfall soon after application may decrease the effectiveness of PENNCAP-M®, and it should not be applied if rainfall is expected within 6 hours of application. At the time of the applications, crop height was approximately 8 feet.

In this study, sweet corn grown in New York were sprayed four times over a nine day period (at 3-day intervals) with PENNCAP-M® at 0.75 pounds ai per acre for each application. Applications were made using the Hagie High Clearance broadcast sprayer delivering approximately 25 gallons per acre. The sprayer was outfitted with eight Flat Fan 8003 nozzles. The nozzle spacing was 18 inches, and the swath width was 12 feet. The equipment was calibrated prior to each application by using the volume/time method for liquid applications and verification data is presented on page 60 of the study report.

**Meteorology**

Historical (1990-1999) meteorological data (page 59 of study report) obtained from National Oceanic & Atmospheric Administration (NOAA) weather station 7842, Sodus Center, New York were presented in the study report. The computerized weather station at the field site was calibrated, however, the computer and software were not validated. The on-site computerized weather station data reported approximately normal temperature conditions (50.1 °F to 75.2 °F) during the trial period. On-site computerized precipitation testing equipment indicates that the test site received approximately one inch less rainfall (2.62 inches) during the study than that reported by historical data during August (3.5 inches). September precipitation (3.75 inches) was approximately the same as historical data. Additional data were presented by the on-site computerized weather station at the time of each application: relative humidity was 80-95 percent, soil temperature at 2 inches was 46 to 80 °F, and at 6 inches was 42 to 74 °F, soil was reported as moist, wind speed and direction was 0-4 mph from the west, and cloud cover was reported as 0 to 100 percent. Meteorology data are presented on page 19 and 61 of the study report.

No overhead irrigation was applied during the treatment period. However, precipitation is reported to have occurred on each day of application (application 1-4) at 0.23, 0.03, 0.03, and 0.04 inches, respectively.

**Sampling of Leaf Dislodgeable Residue Samples**

Sweet corn leaf punch samples were collected prior to and after each of the four applications, 8 hours, and 1, 2, 3, 4, 7, 10, 14, 21, 28, and 35 days after the fourth treatment. However, protocol deviation #2 of the field report states that the 28 day samples were collected on day 27 after the fourth application due to rain predictions for the 28$^{th}$ day sampling event.

At each field test site, leaf punch samples were collected from three subplots in each treated plot. A single leaf punch sample was collected from the control plot at each sampling interval. Field fortification samples were prepared after the first application and after the DAT-1 sampling interval. Dislodging solutions used for spiking were produced by collecting and rinsing control leaf punch samples and fortifying the resulting solution with methyl parathion and methyl paraoxon concentrations. At each spiking event, 15 samples were produced including one control sample. Fortification solutions were provided by Morse Laboratories. The solutions were spiked in duplicate with either methyl parathion or methyl paraoxon at 0.5, 8, 400, or 4,000 $\mu$g/sample (0.00125, 0.02, 1.0, and 10 $\mu$g/cm$^2$). After spiking, the samples were immediately placed into freezer storage.

Samples consisted of a 400 cm$^2$ leaf surface area, counting both sides of the leaf surface. A Birkestrand leaf punch sampler with a 2.523 cm punch diameter was used to collect 40 leaf discs per sample. Leaf disc samples were held in field coolers with blue ice until dislodging. Leaf disc samples were dislodged two times with 100 mL of a 0.01% v/v aqueous solution of

Aerosol® OT. Samples were dislodged on a reciprocating shaker operating at 200 cycles per minute. The dislodging procedure began within four hours of sampling.

**QA/QC**

*Sample Handling and Storage*

After dislodging, the samples were immediately placed into freezer storage at the field facility prior to shipping. All samples were identified and labeled in the field using a unique study number, sample number and sample type. Information on the freezer temperature is not available in the report.

All samples were shipped from the test sites within 1 to 18 days of sample collection. Samples were shipped to the analytical laboratory, Morse Laboratories, Inc., Sacramento, California, on dry ice via FedEx.

Upon arrival at Morse Laboratories, the samples were transferred to a limited-access freezer for storage where they remained until they were thawed for subsampling. Freezer storage temperatures were monitored on a daily basis and were maintained at -20 ± 5 °C.

*Tank Mix and Product Analyses*

Information on tank mix analysis was not provided in the study report. The certified ai content of PENNCAP-M® used on one of the treated plots (Treatment #2, batch # EHP-08M9-11) was 20.2 percent with a certification date of July 10, 2000. The certified ai content of PENNCAP-M® used on the other treated plot (Treatment #3, batch # EHP-02F9-02S) was 20.5 percent with a certification date of July 17, 2000.

*Analytical Methodology*

The analytical methodology used for the determination of methyl parathion and methyl paraoxon concentrations in filtered/non-filtered PENNCAP-M® DFR Aerosol® OT solutions was identified in the report as Morse Laboratories, Inc. Analytical Method No. Meth-121, Revision #3, entitled "Determination of Methyl Parathion and its Oxygen Analog in Dislodgeable Foliar Residue (DFR) Solutions". Modifications to the method, dated September 8, 2000 or October 4, 2000, enabled lowering of the limit of quantification (LOQ) from 0.01 $\mu g/cm^2$ to 0.001 $\mu g/cm^2$. Copies of the methods employed are presented in Appendix I and II of the final analytical report section of the study report. No information on the method validation was provided in this report.

The method is capable of determining the levels of total methyl parathion (free and microencapsulated) and its oxygen analog, methyl paraoxon, in DFR solutions where microencapsulated formulations have been applied.

Samples were analyzed on a non-filtered basis. In addition, selected samples were analyzed after filtration to determine any differences in the amount of residue present in the DFR solution. Unfiltered sample analysis was conducted by adding tetrahydrofuran to a specific volume of dislodging solution (typically 0.01 percent Aerosol® OT in water) to dissolve the encapsulating material of the formulation, releasing the methyl parathion and methyl paraoxon, and also to provide a partition medium for subsequent extraction of the analytes from the aqueous sample. Following sonication, an excess of solid NaC1 was added for solvent separation. An aliquot of the organic phase was removed and purified by means of carbon black solid phase extraction tube cleanup. The resulting purified extract was concentrated then submitted to analysis. Detection and quantification were conducted using the Hewlett Packard gas chromatograph Model 5890 Series II (with HP 7673 Autosampler) and 6890 (with HP 6890 Autosampler) equipped with a flame photometric detection in the phosphorus mode, used in combination with a G2070AA ChemStation. Filtered sample analysis is described on page 89 of the study report.

Standard linearity curves of four standards were generated with regression statistic correlation of $R^2$=0.99 (LOQ = 0.01 and 0.001 $\mu g/cm^2$) for both methyl parathion and methyl paraoxon. Representative chromatograms of standards and fortified samples are provided in the report. Chromatograms show good peak sharpness and separation.

*Limit of Detection (LOD) and Limit of Quantitation (LOQ)*

The analytical methods used for the analysis of methyl parathion and methyl paraoxon had a target limit of detection (LOD) of 0.003 $\mu g/cm^2$ and a target LOQ of 0.01 $\mu g/cm^2$. The method was modified to permit residue determination at a lower LOQ of 0.001 $\mu g/cm^2$ on selected samples.

*Laboratory Recovery*

Freshly-fortified control samples of methyl parathion and methyl paraoxon were analyzed concurrently with each analytical set to monitor the procedural recovery. Each analytical set included one reagent blank, one control sample, two fortified control samples (one at LOQ and one at higher levels), and up to ten field samples (field or field fortified). For the analysis of methyl parathion and methyl paraoxon, fortification levels of 0.01, 0.5, 1, 4, 5, 8, 10, and 400 $\mu g/cm^2$ were analyzed.

For the non-filtration method, having an LOQ of 0.01 $\mu g/cm^2$, methyl parathion recoveries (including fresh fortifications for field fortification runs) ranged from 74 to 99 percent with a mean and standard deviation of 87 percent ± 6.2 (n=22), and methyl paraoxon recoveries (including fresh fortifications for field fortification runs) yielded a range of 74 to 106 percent with a mean and standard deviation of 91 percent ± 8.8 (n=24). Procedural recovery results were corrected for any detectable control contribution

For the non-filtration method, having an LOQ of 0.001 $\mu g/cm^2$, methyl parathion recoveries (including fresh fortifications for field fortification runs) ranged from 72 to 127 percent with a mean and standard deviation of 88 percent ± 11 (n=22). Methyl paraoxon recoveries (including fresh fortifications for field fortification runs) ranged from 76 to 109 percent with a mean and standard deviation of 91 percent ± 9.6 (n=20). Procedural recovery results were corrected for any detectable control contribution.

Filtration method procedural recoveries are discussed on page 100 of the study report.

*Field Fortification Recovery*

Field fortification samples were prepared after the first application and after the 24 hour sampling interval. Dislodging solutions for spiking were produced by collecting and dislodging control plot leaf punch samples.

After each spiking event, 15 samples were produced including one control sample. The solutions were spiked in duplicate with either methyl parathion or methyl paraoxon at 0.5, 8, 400, or 4000 $\mu g$/sample (0.00125, 0.02, 1.0, and 10 $\mu g/cm^2$). Only field fortification samples, whose fortification levels were consistent with the residue levels found in actual field samples were analyzed.

Table 1 summarizes the overall average field fortified sample recovery results. All reported field fortification recoveries were corrected for the mean recovery of concurrently analyzed freshly fortified control samples Recoveries from methyl parathion field fortifications ranged from 81 to 107 percent and yielded a mean and standard deviation of 95 percent ± 7.8 (n=12). Recoveries from methyl paraoxon field fortifications ranged from 87 to 89 percent and yielded a mean and standard deviation of 88 percent ± 1.4 (n=2). Due to a potential error in field fortification of two of the four methyl paraoxon field fortifications samples analyzed, the results from the two suspect samples were not included in the statistical evaluation.

*Storage Stability Recovery*

Storage stability was determined for methyl parathion and methyl paraoxon in DFR solution for the period of frozen storage applicable to this study. Stability samples were prepared and analyzed under the companion study KP-99-16. Storage stability results indicate that methyl parathion and methyl paraoxon are stable in Aerosol® OT DFR solution for up to 168 days, provided the samples are stored frozen (-20 °C ± 5).

Table 1. Summary of Average Field Fortification Recoveries by Fortification Level*

| Test Substance | Fortification Level ($\mu g/cm^2$) | Recovery* (percent) |
|---|---|---|
| Methyl Parathion | 0.00125<br>0.02<br>1.0<br>10 | 94.3 ± 4.5 (N=4)<br>87.5 ± 6.0 (N=4)<br>102.3 ± 6.5 (N=4)<br>N/A |
| | **Overall Average** | 95 ± 7.8 (N=12) |
| Methyl Paraoxon | 0.00125<br>0.02<br>1.0<br>10 | N/A<br>88.0 ± 1.4 (N=2)<br>N/A<br>N/A |
| | **Overall Average** | 88 ± 1.4 (N=2) |

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

**Results**

Average corrected DFR data are summarized in Table 2. The data were corrected using the overall average field fortification recoveries for methyl parathion and methyl paraoxon from the respective field sites (Table 1). Note: the darker-shaded cells indicate analysis or reanalysis occurred using the modified analytical method which had an LOQ of 0.001 $\mu g/cm^2$. No residues above LOQ of 0.01 $\mu g/cm^2$ or 0.001 $\mu g/cm^2$ for methyl parathion and methyl paraoxon were found in any untreated control samples.

The maximum average methyl parathion residue occurred immediately following the 3rd application in Treatment #3 (2.05 $\mu g/cm^2$). Although methyl parathion residues decreased to below the LOQ of 0.001 $\mu g/cm^2$ at DAT-21 in Treatment #2, detectable values in Treatment #3 were found at the last study sampling event DAT-35.

The maximum average methyl paraoxon residue level occurred 8 hours (DAT-0.3) after the fourth application in Treatment #2 (0.0136 $\mu g/cm^2$). Average methyl paraoxon residue levels fell to below LOQ at DAT-1 after the fourth application in Treatment #2 and residue levels in Treatment #3 were less than LOQ at each sampling event after the fourth application.

**Table 2. Summary of Average Corrected DFR Residue Data (Non-Filtered Samples) by Sampling Interval**

| Sampling Interval | Treatment #2 Plot | | | Treatment #3 Plot[b] | |
|---|---|---|---|---|---|
| | Methyl Parathion ($\mu g/cm^2$) | Methyl Paraoxon ($\mu g/cm^2$) | Methyl Parathion and Methyl Paraoxon ($\mu g/cm^2$) | Methyl Parathion ($\mu g/cm^2$) | Methyl Paraoxon ($\mu g/cm^2$) |
| Pre 1st App | <0.001 | <0.001 | <0.001 | <0.001 | <0.001 |
| Post 1st App | 1.06 | 0.0133 | 1.0733 | 1.16 | <0.01 |
| Pre 2nd App | 0.0920 | 0.00133 | 0.0933 | 0.315 | 0.00295 |
| Post 2nd App | 1.55 | <0.01 | 1.55 | 1.28 | <0.01 |
| Pre 3rd App | 0.226 | 0.00349 | 0.2295 | 0.752 | 0.00992 |
| Post 3rd App | 1.95 | <0.01 | 1.95 | 2.05 | <0.01 |
| Pre 4th App | 0.0414 | 0.00117 | 0.0426 | 0.151 | 0.00260 |
| App 4, Hour 0 | 1.47 | <0.01 | 1.475[a] | 0.697 | <0.01 |
| App 4, Hour 8 | 0.866 | 0.0136 | 0.8796 | 0.803 | <0.01 |
| App 4, Day 1 | 0.532 | <0.01 | 0.5370[a] | 0.561 | <0.01 |
| App 4, Day 2 | 0.225 | <0.01 | 0.225 | 0.299 | <0.01 |
| App 4, Day 3 | 0.154 | <0.01 | 0.154 | 0.348 | <0.01 |
| App 4, Day 4 | 0.0885 | <0.01 | 0.0885 | 0.278 | <0.01 |
| App 4, Day 7 | 0.00546 | <0.001 | 0.00546 | 0.0221 | <0.001 |
| App 4, Day 10 | 0.00278 | <0.001 | 0.00278 | 0.0202 | <0.001 |
| App 4, Day 14 | <0.001 | <0.001 | <0.001 | 0.00677 | <0.001 |
| App 4, Day 21 | -- | -- | -- | 0.0254 | <0.001 |
| App 4, Day 27 | -- | -- | -- | 0.00166 | <0.001 |
| App 4, Day 35 | -- | -- | -- | 0.00129 | <0.001 |

Note: the darker-shaded cells indicate analysis or reanalysis occurred using the modified analytical method, which had an LOQ of 0.001 $\mu g/cm^2$. All methyl parathion and methyl paraoxon residues were corrected for corresponding field recoveries.

a For the methyl paraoxon residue value, half of the LOQ (0.01 $\mu g/cm^2$) was added to the methyl parathion residue since measurable levels of methyl paraoxon were found before and after this study period.

b Total methyl parathion and methyl paraoxon residues were not calculated for treatment plot #3, since no methyl paraoxon residue values were above LOQ after the fourth treatment.

*Sample 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. Adjustments in the raw data for methyl parathion and methyl paraoxon were made for the overall average field fortification recoveries (see Table 1). Methyl paraoxon residues were below the LOQ following the final application except for the 0.0136 $\mu g/cm^2$ level at 8 hours after the fourth application, and therefore were not used in regression analysis. Statistical analysis of the residue data was limited to arithmetic mean, standard deviation, and regression analysis.

The study author averaged corrected triplicate DFR values (non-filtered samples) 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 plot beginning with the samples collected immediately after the fourth application 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. Regression analysis of the methyl parathion residue data indicates that the dissipation half-life was 1.1 days ($R^2$=0.97) for methyl parathion at Treatment 2 and 3.7 days ($R^2$=0.84) at Treatment 3.

Versar used individual corrected DFR values (non-filtered samples), not averages, in conducting linear regressions on the data sets. Versar corrected all the field data using the average field fortification recovery values for methyl parathion and methyl paraoxon from the respective plot (Table 1). Only DFR values greater than the LOQ were included, with the exception of Treatment 3, DAT-28 and 35, where, for calculation purposes, the <LOQ (0.001 $\mu g/cm^2$) value of one replicate was given the value of ½ LOQ. The linear regressions were conducted using the natural logarithm of DFR values processed by Microsoft's® Excel 2000. The DFR half-lives, as estimated by Versar, are presented in Table 3. Specifically, for Treatment #2, Versar's half-life was 1.1 days ($R^2$=0.96) and for Treatment #3 data, Versar estimated a slightly shorter half-life of 3.5 days, as compared to the study author's prediction of 3.7 days, with a similar estimated $R^2$ of 0.83.

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. An analysis for the combined residues was only done for treatment #2 plot, not treatment #3 plot, since no methyl paraoxon was found in any sampling interval at the treatment #3 plot. The combined analysis 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. 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. Half of the LOQ (0.01 $\mu g/cm^2$) was also added to the methyl parathion residue on the day of the fourth application since measurable levels of methyl paraoxon were found before and after this study period. Regression analysis of the combined

residue data from treatment #2 plot indicates that the dissipation half-life was 1.1 days, with an $R^2$ value of 0.97. This half life value is the same as the half life values calculated by Versar and the study author for methyl parathion at treatment #2 plot.

**Table 3. Half-lives as Estimated by American Agricultural Services and Versar**

| Data Used for Regression | Treatment #2 Plot | | Treatment #3 Plot | |
|---|---|---|---|---|
| | Methyl Parathion | | Methyl Parathion | |
| | Half-life (days) | $R^2$ | Half-life (days) | $R^2$ |
| American Agricultural Services | 1.1 | 0.97 | 3.7 | 0.84 |
| Versar | 1.1 | 0.96 | 3.5 | 0.83 |
| Total residue | 1.1 | 0.97 | - | - |

## Data Variability

Versar examined data variability as part of the linear regression analyses. Coefficients of variance for methyl parathion replicate sample data, up to the first post application day where all replicate residue values were below the LOQ, ranged from 6.2 to 54.8 percent for Treatment #2 and 7.1 to 144 percent for Treatment #3.

## Compliance Checklist

The itemized checklist below describes compliance with the major technical aspects of the relevant sections of the OPPTS Series 875 Postapplication Exposure Monitoring Test Guidelines Part B.

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

- *Dislodgeble 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 New York and companion studies were conducted in Florida and California (MRID# 45269701). Florida and California ranked one and two in sweet corn production in 1997 and accounted for approximately 43 percent of the total U.S. sweet corn production. New York ranked fourth (7 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 were 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 sampling period of the study represented the summer growing season on into the Fall. The climatological data from both sites indicated no significant departure from the "normal" air temperature and historical rainfall amounts during the trial period.

- *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 not met. A product label was provided in the study report. The label states that the maximum application rate for sweet corn is 4 pints of formulated product per acre or 1.0 pound ai per acre. In this study, sweet corn was sprayed four times during the two weeks prior to harvest with PENNCAP-M® at the rate of 3 pints formulated product per acre or 0.75 pounds ai per acre.

- *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 August and September.

- *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, 3 days apart, were made at each test site.

- *Sampling should be sufficient to cover three half-lives and establish a dissipation curve.* This criterion was met. The sampling interval duration was sufficient to cover a minimum of three half-lives (e.g., 14 days sampling interval for Treatment 2 with a 1.1 day half-life, and 35 day sampling interval for Treatment 3 for a 3.7 day half-life).

- *Meteorological conditions including temperature, wind speed, daily rainfall, and humidity should be provided for the duration of the study.* This criterion was partially met. Air temperature readings, relative humidity, wind speed and direction, cloud cover, and soil moisture and temperature were summarized for days of application only. However, all rainfall events were reported.

- *Residue storage stability, method efficiency (residue recovery), and limit of quantitation (LOQ) should be provided.* These criteria were met. Laboratory, field fortification, and storage recovery values are provided in the study report. The report states the LOQ to be 0.01 $\mu g/cm^2$ with a modified LOQ of 0.001 $\mu g/cm^2$.

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

- *Control and baseline foliar or soil samples collected.* The criterion was met. Control samples were collected from an untreated control plot at each sampling interval.

Other issues and limitations of the data are identified below:

- Irrigation data were not provided. 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 corn crop.