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

OFFICE OF PREVENTION, PESTICIDES AND TOXIC SUBSTANCES

OPP OFFICIAL RECORD
HEALTH EFFECTS DIVISION
SCIENTIFIC DATA REVIEWS
EPA SERIES 361

July 31, 2001

Memorandum

SUBJECT: Review of *Foliar Dislodgeable Residue Dissipation of PENNCAP-M® in Sweet Corn.* (MRID No. 452697-01)

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: D270866 and D271759

Pesticide Chemical Codes: 053501

EPA MRID Numbers: 452697-01 and 452889-01

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 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 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

The insecticide methyl parathion was applied to sweet corn in two geographical locations: Florida and California. A companion sweet corn study was conducted at a later date in New York State (MRID# 45275001). This report also includes a review of the amended final study report which was submitted approximately four months after the original study report (MRID# 45288901). Results from the Florida site, as presented in the original study report, showed rapid dissipation of dislodgeable methyl parathion residues. The amended report provides data generated from the reanalysis of specific samples from the Florida site at a lower limit of quantitation (LOQ), as well as results from an additional storage stability interval to support it. PENNCAP-M®, a flowable formulation consisting of a water suspension of polymeric-type microcapsules which contain 20.9 percent methyl parathion, was applied at both locations. This study was conducted to determine the residue levels of methyl parathion and two metabolites/degradation products, methyl paraoxon and 4-nitrophenol, that can be dislodged from sweet corn foliage following four applications of the test substance, each at an application rate of 0.75 pounds active ingredient (ai) per acre. Applications were made using ground spray equipment at the California site and aerial spray equipment at the Florida site.

Rainfall data at the Florida site was collected at a NOAA Weather Station, 12 miles from the test site. The Florida site received approximately 5 inches of rain during the months of March and April, the trial period. The California site received no rain during the trial period (May and June). Based on the lack of rainfall during the trial period and the moist/wet soil at the time of the applications, it appears that supplemental (furrow) irrigation was used to maintain the health of the sweet corn crop. However, the report provides no information on supplemental irrigation.

Versar used individual DFR values, 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 field site. Only DFR values above LOQ were included in the regression analysis.

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

- Florida Methyl Parathion - 0.4 days ($R^2$=0.95)
- California Methyl Parathion - 4.8 days ($R^2$=0.90)
- California Methyl Paraoxon - 3.8 days ($R^2$=0.79)

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. An analysis for the combined residues was only done for the California site, not the Florida site, since no methyl paraoxon was found in any sampling interval at the Florida site. Regression analysis of the combined residue data from the California site indicates that the dissipation half-life was 4.8 days, with an $R^2$ value of 0.92. This half life value is the same as the half life values calculated by Versar and the study author for methyl parathion at the California site.

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 Florida and California 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.

- The aircraft sprayer used at the Florida site was not calibrated prior to each application.

- 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
100.001-01 File

**FROM:** Kathy Coon/Susan Anderson

**DATE:** February 12, 2001

**SUBJECT:** Review of Foliar Dislodgeable Residue Study: *Foliar Dislodgeable Residue Dissipation of PENNCAP-M® in Sweet Corn*
MRID No. 452697-01

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This report reviews the foliar dislodgeable residue study: *Foliar Dislodgeable Residue Dissipation of PENNCAP-M® in Sweet Corn*, 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 Cerexagri, Inc. (formerly Elf Atochem North America, Inc.). A summary of the study and its compliance with the U.S. EPA's OPPTS Series 875, Occupational and Residential Exposure Test Guidelines, Group B: Postapplication Exposure Monitoring Test Guidelines, 875.2100, Dislodgeable Foliar Residue Dissipation: Agricultural is provided. The following information may be used to identify the study:

| | | |
|---|---|---|
| Study Title: | *Foliar Dislodgeable Residue Dissipation of PENNCAP-M® in Sweet Corn*<br>*361 pages*; Amended Final Study Report 452 pages | |
| Sponsor/Representative: | Elf Atochem North America, Inc.<br>Agrichemicals Division<br>2000 Market Street, 21st Floor<br>Philadelphia, PA 19103-3222 | Rodney Bennett<br>Elf Atochem North America, Inc.<br>900 First Avenue<br>King of Prussia, PA 19406 |
| Field Study Test Sites: | Ron Paden, Principal Investigator<br>Paden Pinnacle Ag Services, Inc.<br>17150 Ave. D<br>Somerton, AZ 85350 (Brawley, CA) | W. Thomas Minter, Principal Investigator<br>Florida Pesticide Research, Inc.<br>1700 Deleon Street<br>Oviedo (Stuart), FL 62765 |
| Analytical Laboratory: | Frances Brookey, Principal Analytical Investigator<br>Morse Laboratories, Inc.<br>1525 Fulton Avenue<br>Sacramento, CA 95825 | |
| Study Director and Author: | Tommy R. Willard, Ph.D.<br>American Agricultural Services, Inc.<br>404 E. Chatham Street<br>Cary, NC 27512 | |
| Report Date: | Original/August 23, 2000 | Amended/December 21, 2000 |
| Identifying Codes: | MRID #452697-01, MRID #452889-01 (Amended Report), Study Number KP-99-16 | |

## 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 two geographical locations: Florida and California. A companion sweet corn study was conducted at a later date in New York State (MRID# 45275001). This report also includes a review of the amended final study report which was submitted approximately four months after the original study report (MRID# 45288901). Results from the Florida site, as presented in the original study report, showed rapid dissipation of dislodgeable methyl parathion residues. The amended report provides data generated from the reanalysis of specific samples from the Florida site at a lower limit of quantitation (LOQ), as well as results from an additional storage stability interval to support it. PENNCAP-M®, a flowable formulation consisting of a water suspension of polymeric-type microcapsules which contain 20.9 percent methyl parathion, was applied at both locations. This study was conducted to determine the residue levels of methyl parathion and two metabolites/degradation products, methyl paraoxon and 4-nitrophenol, that can be dislodged from sweet corn foliage following four applications of the test substance, each at an application rate of 0.75 pounds active ingredient (ai) per acre. Applications were made using ground spray equipment at the California site and aerial spray equipment at the Florida site.

Sweet corn leaf punch samples were collected from treated and control plots in Stuart, Florida (March 15-April 9, 2000) and Brawley, California (May 9-June 15, 2000). In Florida, the sampling was performed prior to the first aerial spray application, immediately after each of the four applications, and 1, 2, 4, 7, and 14 days after the fourth treatment. Sampling was performed in California prior to the first ground spray application, immediately after each of the four applications, 8-12 hours after the fourth application, and 1, 2, 3, 5, 7, 14, 21, and 28 days after the fourth treatment. 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 fortified samples were prepared immediately after the fourth application, four days after the fourth application in Florida and seven days after the fourth application in California.

The maximum average methyl parathion residue at the Florida site occurred immediately after the third treatment (0.9289 $\mu g/cm^2$) and decreased to below the limit of quantitation (LOQ) by the fourth day after the fourth treatment. Reanalysis of specific samples, using a modified analytical method with a lower LOQ, resulted in residue levels below LOQ occurring on the seventh day after the fourth application (0.00127 $\mu g/cm^2$). Average methyl paraoxon residue levels were below LOQ at all sampling intervals, even at the lower LOQ. The maximum average 4-nitrophenol residue level occurred immediately after the fourth treatment (0.0112 $\mu g/cm^2$). All other residue levels of 4-nitrophenol were below LOQ.

In California, the maximum average methyl parathion residue occurred immediately after the fourth treatment (2.2143 $\mu g/cm^2$) and decreased to 0.0331 $\mu g/cm^2$ 28$^{th}$ day after the fourth treatment. No postapplication samples were below LOQ. The maximum average methyl paraoxon residue level occurred 8-12 hours after the fourth treatment (0.0531 $\mu g/cm^3$). Residue levels decreased to below LOQ by the 14$^{th}$ day after the fourth treatment. Residue levels for 4-nitrophenol were below LOQ for the only sampling interval (the fifth day after the fourth treatment). The report states that the climatic differences between the Florida (humid) and California (arid) sites could explain the extended presence of methyl parathion at the California site.

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. Methyl paraoxon levels at the Florida site were consistently below LOQ. Thus, no regression was generated. Likewise, no regressions were generated for 4-nitrophenol because residues were below the LOQ.

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

- Florida - Methyl Parathion - 0.5 days ($R^2$=0.95)
- Florida Methyl Parathion (Modified Method) - 0.7 days ($R^2$=0.89)
- California Methyl Parathion - 4.8 days ($R^2$=0.91)
- California Methyl Paraoxon - 3.9 days ($R^2$=0.94)

Versar used individual DFR values, 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 field site. Only DFR values above LOQ were included in the regression analysis.

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

- Florida Methyl Parathion - 0.4 days ($R^2$=0.95)
- California Methyl Parathion - 4.8 days ($R^2$=0.90)
- California Methyl Paraoxon - 3.8 days ($R^2$=0.79)

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. An analysis for the combined residues was only done for the

California site, not the Florida site, since no methyl paraoxon was found in any sampling interval at the Florida site. Regression analysis of the combined residue data from the California site indicates that the dissipation half-life was 4.8 days, with an $R^2$ value of 0.92. This half life value is the same as the half life values calculated by Versar and the study author for methyl parathion at the California site.

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 Florida and California 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.

- Counter, a soil-applied organophosphate insecticide, was applied to the Florida site at the time of planting. The study protocol states that "all plot areas must not have been treated with organophosphate products within the current growing season of the crop." Two other mantience pesticides were applied to the Florida site during the test period.

- The aircraft sprayer used at the Florida site was not calibrated prior to each application.

- Some of the DFR samples at the Florida site were not dislodged within 4 hours (up to 5.5 hours).

## 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 being 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 armyworms, corn earworms, 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 two metabolites/degradation products, methyl paraoxon (CAS No. 950-35-6) and 4-nitrophenol (CAS No. 100-02-7), 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. Applications were made using ground spray equipment at the Florida site and aerial spray equipment at the California site.

The field portion of the study was conducted at two geographical locations (i.e., Florida and California). A companion sweet corn DFR study (452750-01) was conducted at a later date in New York State. All field and analytical operations were overseen by American Agricultural Services, Inc. of Cary, North Carolina. On-site field operations were conducted by Florida Pesticide Research, Inc. of Oviedo, Florida and Paden Pinnacle Agricultural Services, Inc. of Somerton, Arizona. All DFR leaf samples were analyzed by Morse Laboratories, Inc. of Sacramento, California.

In Florida, leaf punch sampling was performed prior to the first application, immediately after each of the four applications, and 1, 2, 4, 7, and 14 days after the fourth treatment. Aerial spray applications of the test substance at the Florida site were made between March 15 and March 26, 2000. Samples were collected between March 15 and April 9, 2000. Leaf punch sampling was also performed at the California site. Sampling was performed prior to the first application, immediately after each of the four applications, 8-12 hours, and 1, 2, 3, 5, 7, 14, 21, and 28 days after the fourth application. Ground spray applications of the test substance at the California site were made between May 9 and May 18, 2000. Samples were collected between May 9 and June 15, 2000. All dislodged samples were stored frozen for a period ranging from 1 to 64 days before extraction and analysis.

Amended Final Study Report

This report also includes a review of the amended final study report which was submitted approximately four months after the original study report. Results from the Florida site, as presented in the original study report, showed rapid dissipation of dislodgeable methyl parathion

residues. The amended report provides data generated from the reanalysis of specific samples from the Florida site at a lower limit of quantitation (LOQ), as well as results from an additional storage stability interval to support it. Analysis of the samples required modification to the analytical method, as discussed in the original study report. The modified method extended the LOQ for methyl parathion to measurable levels resulting in two additional data points which will determine a more accurate half life. All other methods, materials, equipment, solvents, calculations, procedures, etc. used to conduct the analyses and generate the data presented in the amended study report were the same as described in the original study report. Reanalysis of the specified samples took place up to 165 days following field sampling, and was completed on November 1, 2000. Information from the amended study report are provided in this review where applicable.

**Test Plots**

The field test sites were located in major sweet corn production areas of Florida (Stuart) and California (Brawley). The California site was used exclusively for this DFR study. The Florida site was used concurrently for a sweet corn hand-harvesting worker re-entry exposure study (KP-99-17), as well as this DFR study. (Only the DFR studies are discussed in this review). A treated and an untreated (control) plot were established at each test site. The sweet corn was planted and cultured using normal agronomic practices for sweet corn production in each state. The planting date was December 30, 1999 and January 27, 2000 in Florida and California, respectively. Sweet corn varieties used were *Vail* at the Florida site, and *Zenith* at the California site. Soil types found at each site were sand (Florida) and silty clay (California).

The test site in Florida consisted of a treated plot with a DFR sampling area of 3,210 $ft^2$ (10.7 x 300 feet). This DFR sampling area was within a larger treated area (552,000 $ft^2$) that was used for the worker re-entry study. The treated plot was divided into three replicates (10.7 x 100 feet) to allow for triplicate sampling. Each subplot was 4 rows wide. A two row wide control plot (5.3 x 100 feet) was also established approximately 1 mile east of the treated plot. Sample plot diagrams are provided on pages 67-70 of the study report. Fertilizer was applied to the test site five times, with four applications being made during the growing season.

The test site in California consisted of a treated plot with a DFR sampling area of 3,000 $ft^2$ (30 x 100 feet). The treated plot was divided into 3 replicates (10 x 100 feet) to allow for triplicate samples. A control plot (10 x 100 feet) was established 300 feet north of the treated plot. A sample plot diagram is provided on page 66 of the study report. Fertilizer was applied to the test site three times, with the last application being made approximately 1 month prior to application of the test substance.

**Field and Pesticide Use History**

Sweet corn and cucumber crops were grown in rotation in 1998 and 1999 on the test site in Florida. During this time period, pesticides were applied to the field 55 times. A carbamate insecticide, Lannate (ai = methomyl or S-methyl N-[(methylcarbamoyl)oxy] thioacetimidate) had

been applied 40 times to the test site at a rate of 0.375 pounds per acre. During the course of the current study, eight maintenance pesticides were applied; five as a seed treatment and three during the growing season.

Applications to the test site were made at planting (Counter, organophosphate insecticide, ai = terbufos or S-[[1,1-Dimethylethyl)thio]methyl] O,O-diethyl phosphorodithioate), at early emergence (Pounce Bait, pyrethroid insecticide, ai = permethrin or 3-phenoxybenzyl (1RS)-cis, trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate), and on an as-needed basis (Lannate). The rates of application were not provided in the study report. The study protocol states that "all plot areas must not have been treated with organophosphate products within the current growing season of the crop."

The test site in California was fallow for the three years previous to the current study. No maintenance pesticides were applied to the test site during that time or during the course of the current study.

**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 crop and type of spray equipment. For air applications, a minimum of 2 gallons total spray per acre should be used unless specified otherwise. 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. Rainfall soon after application may decrease the effectiveness of PENNCAP-M®. It should not be applied if rainfall is expected within 6 hours of application.

In this study, sweet corn grown in Florida and California were sprayed four times during the two weeks prior to harvest with PENNCAP-M® at the total nominal rate of 3.0 pounds ai/acre (0.75 pounds ai/acre at each application). Applications at the Florida site were made using aerial spray equipment (Air Tractor Model AT-602) and a broadcast sprayer delivering approximately 5 gallons per acre. The sprayer was outfitted with 10 Micronaire AV-3000 nozzles. The nozzle spacing was 48 inches, and the swath width was 85 feet. The equipment was calibrated prior to the first application only. Calibration data were not available. Verification of the application rate was performed using the amount of spray mix remaining after each application (a deviation from the study protocol). The interval between applications ranged from 3-5 days. At the time of the applications, crop height was 72-84 inches.

Applications at the California site were made using ground spray equipment (tractor) and a broadcast sprayer delivering approximately 30 gallons per acre. The sprayer was outfitted with 6 hollow cone nozzles. The nozzle spacing was 30 inches and the swath width was 15 feet. The

equipment was calibrated (i.e., volume/time) prior to each application. Verification of the application rate was performed using the time-over-plot method. The interval between applications was 3 days. At the time of the applications, the crop height was 60 inches.

**Meteorology**

The study report states that climatological data were collected from instruments located at the test sites and/or permanent recording stations (i.e., NOAA and others). More detailed information is not available in the report. Air temperature readings, relative humidity, wind speed and direction, cloud cover, and soil moisture and temperature are summarized in the report for the days of application at each test site. Monthly air temperature and precipitation data were provided for the two months of application and sampling. Historical meteorological data (monthly air temperature and precipitation) were also provided (1961-90 for California; 1998-99 for Florida). The report states that the climatological data from both sites indicated no significant departure from the "normal" air temperature and historical rainfall amounts during the trial period.

Rainfall data at the Florida site was collected at a NOAA Weather Station, 12 miles from the test site. (The plot diagram indicates a rain gauge at the test site; however, the report states that rainfall data were obtained from a NOAA station.) The Florida site received approximately 5 inches of rain during the months of March and April, the trial period. A total of 0.15 inches of rainfall occurred on the day of the first application. A total of 1.18 inches of rain fell during sampling period after the fourth application. Air temperatures during the months of March and April ranged from 62°F to 82°F. Climatic conditions reported on the days of application show air temperatures ranging from 74°F to 86°F, moist surface soils, relative humidities of 22 to 66 percent, and winds 0 to 8 mph. The 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 sweet corn crop.

The California site received no rain during the trial period (May and June). Air temperatures during the months of May and June ranged from 62°F to 104°F. Climatic conditions reported on the days of application show air temperatures ranging from 69°F to 94°F, moist to wet surface soils, relative humidities of 25 to 40 percent, and winds 0 to 6 mph. No overhead irrigation was used after the test applications and sampling began. Based on the lack of rainfall during the trial period and the moist/wet soil at the time of the applications, it appears that supplemental (furrow) irrigation was used to maintain the health of the sweet corn crop. However, the report provides no information on supplemental irrigation.

**Sampling of Leaf Dislodgeable Residue Samples**

Sweet corn leaf punch samples were collected at the following intervals in Florida: prior to the first application, immediately after each of the four applications, and 1, 2, 4, 7 and 14 days after the fourth treatment. Samples were collected at the following intervals in California: prior to the first application, immediately after each of the four applications, 8-12 hours after the fourth

application, and 1, 2, 3, 5, 7, 14, 21, and 28 days after the fourth treatment. Samples could not be collected after the 28th day following the fourth application, as planned, due to normal leaf drop. 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 fortification samples were prepared immediately after the fourth application (one day after the fourth application at Florida site, a deviation from the protocol), and four days (Florida) and seven days (California) after the fourth application. Dislodging solutions used for spiking were produced by collecting and rinsing additional control leaf punch samples and fortifying the resulting solution with methyl parathion and methyl paraoxon. Information on the sampling approach utilized were not provided in the report.

Samples consisted of a 405 $cm^2$ leaf surface area, counting both sides of the leaf surface. A Birkestrand leaf punch sampler with a 1.0 inch punch diameter was used to collect 40 leaf discs per sample. Leaf disc samples were transported and held in coolers with blue ice until dislodging. Leaf disc samples were dislodged two times with 100 mL of a 0.01 percent v/v aqueous solution of the wetting agent Aerosol® OT 75 (dioctyl sodium sulfosuccinate). The dislodging procedure generally began within four hours of sampling. However, leaf discs were held up to 5.5 hours at the Florida site. After dislodging, the samples were immediately placed into freezer storage. Details on the sample dislodging procedures were not provided in the report.

**QA/QC**

*Sample Handling and Storage*

At the field test sites, leaf punch samples were dislodged with 0.01 percent Aerosol® OT 75. After dislodging, the leaf discs were discarded and the dislodging solution samples were immediately placed into freezer storage. Samples remained frozen throughout storage at the field test sites (Information on the freezer temperature is not available in the report).

All samples were shipped from the test sites within 3 to 44 days of sample collection. Samples were shipped to the analytical laboratory, Morse Laboratories, Inc., in Sacramento, California, via FedEx on dry ice or via ACDS freezer trucking service. All samples were identified with a unique sample number containing the study number, site identifier and a serial number.

Upon arrival at Morse Laboratories, having been anywhere from 1 to 18 days in transport, the samples were transferred to a limited-access freezer for storage where they remained until 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® was 21.1 percent (December 29, 1999). A re-analysis was completed on December 10, 2000.

*Analytical Methodology*

Morse Laboratories, Inc. analyzed samples of the Aerosol® OT-75 dislodging solution used to surface extract sweet corn 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 methodologies used for the PENNCAP-M® DFR analysis were identified in the report as: Morse Laboratories, Inc. Analytical Method No. Meth-121, Original, and Revisions #2 and #3, dated November 11, 1999, May 2, 2000, and May 12, 2000, and entitled, "Determination of Methyl Parathion and its Oxygen Analog in Dislodgeable Foliar Residue (DFR) Solutions" and Morse Laboratories, Inc. Analytical Method No. Meth-126, dated May 11, 2000, entitled, "Determination of 4-Nitrophenol in Dislodgeable Foliar Residue (DFR) Solutions." Copies of the methods employed are presented in Appendix I and II of the study report. The report states that validation of the methods was successful (pages 320, 329). No additional information on the validation studies was provided in this report.

Methyl Parathion and Methyl Paraoxon:

*Analytical Method-121* was used for the analysis of methyl parathion and methyl paraoxon in DFR solutions. To a specific volume of dislodging solution, tetrahydrofuran was added to: 1) dissolve the encapsulating material of the formulation, thereby releasing the methyl parathion (and any methyl paraoxon) contained within; and 2) provide a partition medium for subsequent extraction of the analytes from the aqueous sample. Sonication was employed to achieve maximum recovery of the analytes from the microcapsules. 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 resulting purified extract was concentrated then submitted to analysis.

Samples were analyzed using a Hewlet Packard 5890 Series II gas chromatograph employing flame photometric detection (FPD) in the phosphorus mode. The typical run time was approximately 10 minutes and the typical retentions times were approximately 5.4 and 5.6 minutes for methyl parathion and methyl paraoxon, respectively. A complete listing of typical instrument conditions is provided in the report. Four analytical standards were used for the analyses and standard linearity curves were generated. Regression statistics indicate an excellent correlation ($R^2$=0.99) for both methyl parathion and methyl paraoxon. Representative chromatograms of standards and fortified samples are provided in the report. Chromatograms show good peak separation and sharpness of peaks.

Revisions to Method-121 are reported in Revision #2 and #3 dated May 2, 2000 and May 12, 2000, respectively. Revisions include reducing the N-Evap final concentration volume (#2), eliminating the acetone exchange (#3), and providing an alternate SPE tube processing system (#3). These revisions to the method were made after the analysis had been completed for some Florida samples, but before analysis of the California samples had been initiated.

4-Nitrophenol

*Analytical Method-126* was used for the analysis of 4-nitrophenol in DFR solutions. The 4-nitrophenol (a degradation product of several organophosphate insecticides including methyl parathion) was isolated from the DFR dislodging solution 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 Hewlet Packard 5890E gas chromatograph employing mass selective detection. The typical retention time was 15.0 minutes (run time was not provided). The actual retention times varied up to approximately 2 minutes indicating that the operating conditions could not be maintained consistently. A complete listing of typical instrument conditions is provided in the report. Four analytical standards were used for the analyses and standard linearity curves were generated. Regression statistics indicate an excellent correlation ($R^2$=0.99) for 4-nitrophenol. Representative chromatograms of standards and fortified samples are provided in the report. Chromatograms show good peak separation and reasonably sharp peaks.

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The analytical method used for the analysis of methyl parathion and methyl paraoxon in DFR solutions was Morse Laboratories, Inc. Analytical Method No. Meth-121, entitled, "Determination of Methyl Parathion and its Oxygen Analog in Dislodgeable Foliar Residue (DFR) Solutions," Revision #4. As written, the analytical method is capable of detecting and quantifying residues to a LOQ of 0.01 $\mu$g/cm$^2$. The method modifications, dated September 8, 2000 and October 4, 2000, permitted detection and quantification of residues down to a lower LOQ of 0.001 $\mu$g/cm$^2$. Pertinent modifications are noted on page 28 of the amended study report.

Samples were still analyzed using a Hewlet Packard 5890 Series II gas chromatograph employing FPD in the phosphorous mode. Instrument conditions are not provided in the amended study report. The concentration of the lowest calibration standard was changed from 0.012 $\mu$g/mL to 0.008 $\mu$g/mL. Regression statistics indicate an excellent correlation ($R^2$=0.99) for both methyl parathion and methyl paraoxon. Representative chromatograms of standards and fortified samples are provided in the amended study report. Chromatograms show good peak separation and sharpness of peaks.

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

The analytical methods used for the analysis of methyl parathion and methyl paraoxon, as well as 4-nitrophenol, had a target LOQ of 0.01 $\mu g/cm^2$. The target limit of detection (LOD) was reported as 0.003 $\mu g/cm^2$.

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The modified analytical method used for the analysis of methyl parathion and methyl paraoxon had a target LOQ of 0.001 $\mu g/cm^2$. The target LOD was 0.0003 $\mu g/cm^2$.

*Laboratory Recovery*

Freshly-fortified control samples were analyzed concurrently with each set of field samples to monitor the procedural recovery of both methyl parathion and methyl paraoxon, and 4-nitrophenol. Five fortification levels were prepared, but only two fortified control samples were analyzed, along with a control sample, with each set of field samples. For the analysis of methyl parathion and methyl paraoxon, fortification levels were 0.01, 0.5, 1.0, 5.0, and 9.9 $\mu g/cm^2$; 4-nitrophenol levels were 0.01 and 0.5 $\mu g/cm^2$.

Overall methyl parathion recoveries (including fresh fortifications for field fortification and storage stability runs) yielded a mean and standard deviation of 92 percent ± 9.1 (n=46) and ranged from 74 to 114 percent. Overall methyl paraoxon recoveries (including fresh fortifications for field fortification and storage stability runs) yielded a mean and standard deviation of 97 percent ± 11 (n=46) and ranged from 81 to 130 percent. Overall 4-nitrophenol recoveries yielded a mean and standard deviation of 86 percent ± (n=12) and ranged from 65 to 103 percent. Recovery results were corrected for any detectable control contribution.

To determine the method's efficiency at quantitatively recovering methyl parathion from the microcapsules in the PENNCAP-M® formulated product contained in DFR solution, control samples were fortified with a water suspension of PENNCAP-M® at two different levels and were analyzed as routine samples. Overall recoveries for methyl parathion from the formulated product yielded a mean and standard deviation of 94 percent ± 7.6 (n=9) and ranged from 84 to 107 percent.

To monitor procedural recovery of methyl parathion in the presence of dissolved formulated product microcapsules and other inert ingredients, control samples (DFR solution) were fortified with formulated product in which the microcapsules were first dissolved in a small amount of tetrahydrofuran (THF) then brought to a known volume in acetone. These fortifications were conducted and analyzed concurrently with routine samples of approximately every fourth analytical set. The overall recoveries for methyl parathion from these fortifications yielded a mean and standard deviation of 98 percent ± 13 (n=2) and ranged from 89 to 108 percent.

Freshly fortified control samples (0.001 and 0.01 $\mu g/cm^2$) were analyzed with the analytical set to determine the procedural recovery of both methyl parathion and methyl paraoxon using the modified analytical procedure. Overall methyl parathion recoveries yielded a mean and standard deviation of 90 percent ± 2.8 (n=2) and ranged from 88 to 92 percent. Overall methyl paraoxon recoveries yielded a mean and standard deviation of 107 percent ± 11 (n=2) and ranged from 99 to 115 percent.

*Field Fortification Recovery*

Field fortification samples were prepared using methyl parathion or methyl paraoxon. No field fortifications were conducted using 4-nitrophenol. The samples were prepared immediately after the fourth application at both sites (one day after the fourth treatment at Florida site, a deviation from the protocol), and on fourth day after the fourth treatment (Florida site) and the seventh day after the fourth treatment (California site). The dislodging solutions used for the fortifications were produced by collecting and rinsing control plot leaf punch samples. The solutions were fortified in duplicate at approximately 0.02, 1.0, and 10 $\mu g/cm^2$. A total of 12 samples were produced at each spiking event. Only 6 of the fortified samples were analyzed from the California site (see protocol amendment #2, p. 343 of study report).

Table 1 summarizes the overall average corrected field fortified sample recovery results. The results were corrected for procedural recovery. All DFR data for methyl parathion and methyl paraoxon were corrected for field recoveries by the study author. Although, the recoveries at the 1.0 $\mu g/cm^2$ (86 percent) and 10 $\mu g/cm^2$ (78 percent) fortification levels for the California samples were the only ones in the range of values which must be corrected (i.e., <90 percent) for recovery according to Guideline 875.2900.

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

| Test Substance | Fortification Level ($\mu g/cm^2$) | Florida (percent) | California (percent) |
|---|---|---|---|
| Methyl Parathion | 0.02 | 95.5 ± 12.6 (N=4) | 102 ± 12.0 (N=2) |
| | 1.0 | 95.0 ± 5.7 (N=4) | 96.5 ± 14.8 (N=2) |
| | 10 | 99.2 ± 8.2 (N=4) | 94.5 ± 16.3 (N=2) |
| | **Overall Average** | 96.6 ± 8.8 (N=12) | 97.5 ± 11.7 (N=6) |
| Methyl Paraoxon | 0.02 | 92.8 ± 9.8 (N=4) | 105 ± 9.9 (N=2) |
| | 1.0 | 104.5 ± 15.6 (N=4) | 85.5 ± 9.2 (N=2) |
| | 10 | 99.0 ± 7.0 (N=4) | 78.0 ± 15.6 (N=2) |
| | **Overall Average** | 98.8 ± 11.5 (N=12) | 89.5 ± 15.5 (N=6) |

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

Freshly fortified control samples (0.001 and 0.01 $\mu g/cm^2$) were analyzed with the analytical set to determine the procedural recovery of both methyl parathion and methyl paraoxon using the modified analytical procedure. Overall methyl parathion recoveries yielded a mean and standard deviation of 90 percent ± 2.8 (n=2) and ranged from 88 to 92 percent. Overall methyl paraoxon recoveries yielded a mean and standard deviation of 107 percent ± 11 (n=2) and ranged from 99 to 115 percent.

*Field Fortification Recovery*

Field fortification samples were prepared using methyl parathion or methyl paraoxon. No field fortifications were conducted using 4-nitrophenol. The samples were prepared immediately after the fourth application at both sites (one day after the fourth treatment at Florida site, a deviation from the protocol), and on fourth day after the fourth treatment (Florida site) and the seventh day after the fourth treatment (California site). The dislodging solutions used for the fortifications were produced by collecting and rinsing control plot leaf punch samples. The solutions were fortified in duplicate at approximately 0.02, 1.0, and 10 $\mu g/cm^2$. A total of 12 samples were produced at each spiking event. Only 6 of the fortified samples were analyzed from the California site (see protocol amendment #2, p. 343 of study report).

Table 1 summarizes the overall average corrected field fortified sample recovery results. The results were corrected for procedural recovery. All DFR data for methyl parathion and methyl paraoxon were corrected for field recoveries by the study author. Although, the recoveries at the 1.0 $\mu g/cm^2$ (86 percent) and 10 $\mu g/cm^2$ (78 percent) fortification levels for the California samples were the only ones in the range of values which must be corrected (i.e., <90 percent) for recovery according to Guideline 875.2900.

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

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| | 1.0 | 95.0 ± 5.7 (N=4) | 96.5 ± 14.8 (N=2) |
| | 10 | 99.2 ± 8.2 (N=4) | 94.5 ± 16.3 (N=2) |
| | **Overall Average** | 96.6 ± 8.8 (N=12) | 97.5 ± 11.7 (N=6) |
| Methyl Paraoxon | 0.02 | 92.8 ± 9.8 (N=4) | 105 ± 9.9 (N=2) |
| | 1.0 | 104.5 ± 15.6 (N=4) | 85.5 ± 9.2 (N=2) |
| | 10 | 99.0 ± 7.0 (N=4) | 78.0 ± 15.6 (N=2) |
| | **Overall Average** | 98.8 ± 11.5 (N=12) | 89.5 ± 15.5 (N=6) |

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

*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 by fortifying 200 mL of a control sample DFR solution at 0.5 $\mu g/cm^2$ with either methyl parathion or methyl paraoxon. The samples were then placed in frozen storage at -20°C ± 5. Duplicate analysis for each analyte was conducted at 0-day, 1-month (31 days), 72 days and 83 days (the longest period of storage). In addition, fortified and unfortified control samples were analyzed concurrently with the stability samples at each analysis interval to determine procedural recovery. The storage stability results were corrected for procedural recovery. No storage stability assessments were made for 4-nitrophenol (see protocol amendment #9, p. 340 of study report). Corrected recoveries ranged from 107 to 113 percent for methyl parathion and 91 to 116 percent for methyl paraoxon.

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Storage stability was determined for methyl parathion and methyl paraoxon in DFR solution based on 168 days of frozen storage (a period longer than the longest storage period for many of the field samples). The average corrected recoveries (corrected for procedural recovery) for the additional stored samples was 100 percent for methyl parathion and 94.1 percent for methyl paraoxon.

**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). No residues above LOQ of methyl parathion, methyl paraoxon, or 4-nitrophenol were found in any untreated control samples or pre-application samples.

The maximum average methyl parathion residue at the Florida site occurred immediately after the third treatment (0.9289 $\mu g/cm^2$) and decreased to below the LOQ by fourth day after the fourth application. Average methyl paraoxon residue levels were below LOQ at all sampling intervals. The maximum average 4-nitrophenol residue occurred on the day of the fourth application (0.0112 $\mu g/cm^2$). All other residue levels of 4-nitrophenol were below LOQ. Residue levels of 4-nitrophenol were not corrected.

In California, the maximum average methyl parathion residue occurred immediately after the fourth treatment (2.2143 $\mu g/cm^2$) and decreased to 0.0331 $\mu g/cm^2$ on the 28$^{th}$ day after the fourth treatment. No postapplication samples were below LOQ. The maximum average methyl paraoxon residue level occurred 8-12 hours after the fourth treatment (0.0531 $\mu g/cm^3$). Residue levels decreased to below LOQ by 14$^{th}$ day after the fourth treatment. Residue levels for 4-nitrophenol were below LOQ for the one sampling interval where data were collected. The

report states that the climatic differences between the Florida (humid) and California (arid) sites could explain the extended presence of methyl parathion at the California site.

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Average corrected DFR data for the reanalyzed samples collected at two sampling intervals in Florida are also summarized in Table 2. The data were corrected using the overall average field fortification values from the Florida site (See Table 1). No residues above the revised LOQ of 0.001 $\mu g/cm^2$ were found in any reanalyzed untreated control samples. The average methyl parathion residues on the fourth and the seventh day after the fourth treatment (based on the modified analytical method) were 0.00338 $\mu g/cm^2$ and 0.00127 $\mu g/cm^2$, respectively. Average methyl paraoxon residue levels remained below LOQ at both sampling intervals.

**Table 2. Summary of Average Corrected DFR Residue Data by Sampling Interval**

| Sampling Interval | Florida (Original Study Report) | | Florida (Amended Report) | | California (Original Study Report) | | |
|---|---|---|---|---|---|---|---|
| | Methyl Parathion ($\mu g/cm^2$) | Methyl Paraoxon ($\mu g/cm^2$) | Methyl Parathion ($\mu g/cm^2$) | Methyl Paraoxon ($\mu g/cm^2$) | Methyl Parathion ($\mu g/cm^2$) | Methyl Paraoxon ($\mu g/cm^2$) | Methyl Parathion and Methyl Paraoxon ($\mu g/cm^2$) |
| Pre-Application | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| App #1, Hour 0 | 0.8887 | <0.01 | 0.8887 | <0.01 | 0.9602 | 0.0137 | 0.9739 |
| App #2, Hour 0 | 0.6526 | <0.01 | 0.6526 | <0.01 | 1.1429 | 0.0259 | 1.1688 |
| App #3, Hour 0 | 0.9289 | <0.01 | 0.9289 | <0.01 | 1.8469 | 0.0488 | 1.8957 |
| App #4, Hour 0 | 0.8505 | <0.01 | 0.8505 | <0.01 | 2.2143 | 0.0504 | 2.2647 |
| App #4, Hour 8-12 | -- | -- | -- | -- | 1.5204 | 0.0531 | 1.5735 |
| App #4, Day 1 | 0.2691 | <0.01 | 0.2691 | <0.01 | 1.1735 | 0.0453 | 1.2188 |
| App #4, Day 2 | 0.0242 | <0.01 | 0.0242 | <0.01 | 0.7735 | 0.0499 | 0.8234 |
| App #4, Day 3 | -- | -- | -- | -- | 0.6724 | 0.0429 | 0.7153 |
| App #4, Day 4 | <0.01 | <0.01 | 0.00348 | <0.001 | -- | -- | -- |
| App #4, Day 5 | -- | -- | -- | -- | 0.3051 | 0.0156 | 0.3207 |
| App #4, Day 7 | <0.01 | <0.01 | 0.00127 | <0.001 | 0.2541 | 0.0182 | 0.2723 |
| App #4, Day 14 | <0.01 | <0.01 | <0.01 | <0.01 | 0.0880 | <0.01 | 0.093 |
| App #4, Day 21 | -- | -- | -- | -- | 0.0553 | <0.01 | 0.0553 |
| App #4, Day 28 | -- | -- | -- | -- | 0.0331 | <0.01 | 0.0331 |
| App #4, Day 35 | -- | -- | -- | -- | -- | -- | -- |

LOQ = 0.01 $\mu g/cm^2$

Values shown in shaded area were reanalyzed using the modified analytical method with a lower LOQ (0.001 $\mu g/cm^2$).

All methyl parathion and methyl paraoxon residues were corrected for corresponding field recoveries.

*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. A standard curve based on non-linear regression was used to calculate 4-nitrophenol residue levels. Adjustments to the raw data for methyl parathion and methyl paraoxon were made for the overall average field fortification recoveries (see Table 1). No adjustments to 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 were 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 when 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. Methyl paraoxon levels at the Florida site were consistently below LOQ. Thus, no regression was generated. Likewise, no regressions were generated for 4-nitrophenol because residues were below the LOQ. Regression analysis of the residue data indicates that the dissipation half-life was 0.5 days for methyl parathion at the Florida site, 4.8 days for methyl parathion at the California site, and 3.9 days for methyl paraoxon at the California site. The differences in humidity may again explain the nearly ten-fold difference in the methyl parathion half-life between the two sites.

Versar used individual DFR values, not averages, in conducting linear regressions on the three data sets (Appendix A of this review). Versar corrected all of the field data using the average field fortification recovery values for methyl parathion and methyl paraoxon from the respective field site (Table 1). Only DFR values above LOQ were included. 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. Versar's values differ very little from those presented in the study. The correlation coefficients for the regressions ranged from 0.79 to 0.95 for both test sites.

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 the California site, not the Florida site, since no methyl paraoxon was found in any sampling interval at the Florida site. 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. Regression analysis of the combined residue data from the

California site indicates that the dissipation half-life was 4.8 days, with an $R^2$ value of 0.92. This half life value is the same as the half life values calculated by Versar and the study author for methyl parathion at the California site.

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Regression analysis of the corrected residue data presented in Table 2 indicate that the dissipation half-life differed very little from those presented in the original study report for methyl parathion (0.7 days vs. 0.5 days). The correlation coefficient for the regression analysis was slightly lower than that presented in the original study report ($R^2$=0.89 vs. 0.95). Methyl paraoxon levels at the Florida site remained less than LOQ.

*Data Variability*

Versar examined data variability as part of the linear regression analyses. Coefficients of variance for the replicate sample data, up to the first post application day where all replicate residue values were below the LOQ, ranged from 14.4 to 17.8 percent for methyl parathion (Florida); 2.05 to 16.1 percent for methyl parathion (California) and 1.62 to 15.1 percent for methyl paraoxon (California).

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

| Data Used for Regression | Florida (Original Study Report) | | | | California | | | |
|---|---|---|---|---|---|---|---|---|
| | Methyl Parathion | | Methyl Paraoxon | | Methyl Parathion | | Methyl Paraoxon | |
| | Half-life (days) | $R^2$ | Half-life (days) | $R^2$ | Half-life (days) | $R^2$ | Half-life (days | $R^2$ |
| American Agricultural Services[a] | 0.5 | 0.95 | NA | NA | 4.8 | 0.91 | 3.9 | 0.94 |
| Versar[b] | 0.4 | 0.95 | NA | NA | 4.8 | 0.90 | 3.8 | 0.79 |

NA: Not applicable because methyl paraoxon residue levels were consistently <LOQ (<0.01 $\mu g/cm^2$).

a Day 0 to Day 4 after the fourth application for Florida regression; Day 0 to Day 28 after the fourth application for methyl parathion/California regression; and Day 0 to Day 14 after the forth application for methyl paraoxon/California regression. DFR values corrected using average field fortification recovery values. Values <LOQ = ½ LOQ.

b Day 0 to Day 2 after the fourth application for Florida regression; Day 0 to Day 28 after the fourth application for methyl parathion/California regression; and Day 0 to Day 7 after the fourth application for methyl paraoxon/California regression. DFR values corrected using average field fortification recovery values. Only values > LOQ included.

*Compliance Checklist*

Compliance with OPPTS Series 875, Occupational and Residential Exposure Test Guidelines, Group B: Postapplication Exposure Monitoring Test Guidelines, 875.2100, Dislodgeable Foliar 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" used for study review by the U.S. EPA/OPP/HED.

- *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 Florida and California for this study. A companion study (KP-2000-08) was conducted in New York State. These geographic sites were appropriate locations as 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, 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 times chosen for the study represented the spring/early summer growing season. 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 <u>not</u> 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 grown in Florida and California were sprayed four times during the two weeks prior to harvest with Penncap-M® at the rate of 3 pints 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 March (Florida) and in May (California). The fourth and final applications were made 4-5 days prior to harvest and 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, 3-5 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. In Florida, DFR samples were collected prior to the first application, immediately after each of the four applications, and 1, 2, 4, 7 and 14 days after the fourth application. Sampling in California was performed prior to the first application, immediately after each of the four applications, 8-12 hours and 1, 2, 3, 5, 7, 14, 21, and 28 days after the fourth application. Samples could not be collected after 28 days after the fourth application, as planned in California, due to normal senescence. Half-life values were 0.5 days for methyl parathion in Florida, 4.8 days for methyl parathion in California, and 3.9 days for methyl paraoxon in California. Methyl paraoxon residue levels were below LOQ at all sampling intervals in Florida. The dissipation curve for Florida was refined when specific samples initially quantified as less than the LOQ (the fourth and the seventh day after the fourth application) were reanalyzed using a modified method. The revised half-life value for methyl parathion was 0.7 days.

- *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. Rainfall data at the Florida site was collected from a NOAA station 12 miles from the test site. The report provides no information on supplemental irrigation other than the statement that no overhead irrigation was used after the test applications and sampling began.

- *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 $\mu g/cm^2$. The modified analytical method used for the analysis of methyl parathion and methyl paraoxon in specified samples had a target 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 should be collected.* The criterion was met. Control samples were collected from an untreated control plot at each sampling interval.