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

OFFICE OF PREVENTION,
PESTICIDES AND
TOXIC SUBSTANCES

August 15, 2001

Memorandum

SUBJECT: Review of Foliar and Soil Dislodgeable Residue Study: *Foliar and Soil Dislodgeable Residue Dissipation of Methyl Parathion Residues Following Applications of Penncap-M® Microencapsulated Insecticide on Walnuts* (MRID # 453592-01 and 454009-01 amended)

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

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

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

DP Barcode: D273699 and D274880

Pesticide Chemical Codes: 053501

EPA MRID Numbers: 453592-01 and 454009-01

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 May 4, 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) and soil residue dissipation (SRD) study submitted by Cerexagri, Inc. (formerly Elf Atochem North America, Inc.) in response to the EPA Agricultural Reentry Data Call-In issued on October 18, 1995 and amended January 1997. The insecticide methyl parathion was applied to walnuts in three geographical locations in southern California. The study was conducted in California only, because Penncap-M® has a Section 24(c), Special Local Needs label and is used to control codling moth, navel orange worm, San Jose scale, and walnut scale and almost 100 percent of commerical walnuts are grown in California. Penncap-M®, a flowable formulation consisting of a water suspension of polymeric-type microcapsules which contain 20.9 percent methyl parathion, was applied at all locations. This study was conducted to determine the residue levels of methyl parathion and its oxygen analog, methyl paraoxon, that can be dislodged from walnut foliage and soil following four applications of the test substance, each at the maximum application rate of 2 pounds ai per acre. All applications were made using ground airblast application equipment.

The maximum average dislodgeable foliar methyl parathion residues occurred immediately after the fourth application in Fresno and Ripon, and immediately after the first application in Porterville. Average residue levels after the fourth application were: (1) Fresno - 2.89 $\mu g/cm^2$; (2) Ripon - 2.76 $\mu g/cm^2$; and (3) Porterville - 0.947 $\mu g/cm^2$. Residue levels did not decline below the LOQ (0.01 or 0.001 $\mu g/cm^2$) at any of the sites. Methyl paraoxon residue levels were much lower than methyl parathion residue levels. Average methyl paraoxon residue levels after the fourth application were all below the LOQ (0.01 $\mu g/cm^2$). Residue levels remained below the LOQ (0.01 $\mu g/cm^2$) throughout the sampling period at Ripon, but were intermittently detected above the LOQ (0.01 or 0.001 $\mu g/cm^2$) at various sampling intervals at the other two test sites.

The maximum average dislodgeable soil methyl parathion residues occurred immediately after the third application in Fresno (341 $\mu g/g$), the first application in Ripon (165 $\mu g/g$), and the fourth application in Porterville (91.8 $\mu g/g$). Residues were corrected for moisture content. Average methyl parathion residue values after the fourth application were 65.8 $\mu g/g$ (Fresno), 21.6 $\mu g/g$ (Ripon), and 91.8 $\mu g/g$ (Fresno). The average residue values varied significantly from site to site following each application. Residue values did not decline below the LOQ at any of the sites. Methyl paraoxon residue levels were much lower than methyl parathion residue levels. Average methyl paraoxon residue levels after the fourth application were all below the LOQ (0.5 $\mu g/g$). Residue levels remained below the LOQ (0.5 or 0.05 $\mu g/g$) throughout the sampling

period at Fresno and Ripon, but were detected 8 hours after the fourth applicaton in Porterville (0.875 μg/g) before they declined below the LOQ. The maximum average methyl paraoxon residues occurred immediately prior to the third application in Fresno (3.09 μg/g), immediately after the second application in Ripon (2.73 μg/g), and 8 hours after the fourth applicaton in Porterville (0.875 μg/g).

Versar used average DFR and SRD values in conducting linear regressions for the three test sites. The regressions were performed using the total residue level in each sample (sum of methyl parathion and methyl paraoxon), since methyl parathion and methyl paraoxon are assumed to have the same toxicity. If a residue level was less than the LOQ, then a value one-half of the LOQ was used to calculate the sum of total residues in selected samples. DFR and SRD values beginning with the samples collected immediately after the fourth application through the last day of sampling were included. Data reported as total μg of analyte per gram of soil (corrected for soil moisture) were used in the SRD regressions.

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

<u>DFR Residues - Total Residue</u>

- Fresno 7.78 days ($r^2 = 0.80$)
- Ripon 5.41 days ($r^2 = 0.80$)
- Porterville 6.46 days ($r^2 = 0.84$)

<u>SRD Residues - Total Residue</u>

- Fresno 5.41 days ($r^2 = 0.88$)
- Ripon 8.21 days ($r^2 = 0.81$)
- Porterville 4.41 days ($r^2 = 0.87$)

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

- The overall field fortification recovery for DFR samples of methyl paraoxon from Ripon (66 ± 48 percent) showed a high degree of scatter. The study author stated that the reason for the scatter is unknown, however, it is possible that field fortification techniques may have been a contributing factor, as indicated in the field raw data for this site.

- Rainfall occurred on 2nd and 14th day after the fourth application in Ripon, and on 7th and 10th day after the fourth application in Porterville.

- At the Ripon test site, leaf punch samples could not be collected after the 21st day after the fourth application because of premature leaf loss.

- Tank mix analyses were not performed at any of the test sites. Therefore, it was not possible to verify whether tank mix concentrations were comparable between the three test sites.

MEMORANDUM

TO:	Renee Sandvig	cc: Al Nielsen Margarita Collantes 100.001-01 File L. Phillips
FROM:	Kathy Coon/Pat Wood	
DATE:	May 4, 2001	
SUBJECT:	Review of Foliar and Soil Dislodgeable Residue Study: *Foliar and Soil Dislodgeable Residue Dissipation of Methyl Parathion Residues Following Applications of Penncap-M® Microencapsulated Insecticide on Walnuts* MRID # 453592-01 and 454009-01 amended)	

This report reviews the foliar and soil dislodgeable residue study: *Foliar and Soil Dislodgeable Residue Dissipation of Methyl Parathion Residues Following Applications of Penncap-M® Microencapsulated Insecticide on Walnuts*, submitted by Cerexagri, Inc. (formerly Elf Atochem North America, Inc.), in response to the EPA Agriculture Reentry Data Call-In issued on October 18, 1995 and amended January 1997. 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, Foliar Dislodgeable Residue Dissipation: Agricultural, and 875.2200, Soil Residue Dissipation, and Part C: Quality Assurance/Quality Control is provided. The following information may be used to identify the study:

Study Title:	*Foliar and Soil Dislodgeable Residue Dissipation of Methyl Parathion Residues Following Applications of Penncap-M® Microencapsulated Insecticide on Walnuts* *711 pages*; 3 Volumes
Sponsor:	Cerexagri, Inc. (formerly Elf Atochem North America, Inc.) Agrichemicals Division 2000 Market Street, 21st Floor Philadelphia, PA 19103-3222
Field Study Test Sites and Principal Investigators:	Brian Lange Excel Research Services, Inc. 3021 W. Dakota Ave., Suite 110 Fresno, CA 93722 Laurie Bayramian Plant Sciences, Inc. 9715 Sedan Ave. Manteca (Ripon), CA 95336 Dave Ennes Research For Hire 1696 S. Leggett Street Porterville, CA 93257
Analytical Laboratory:	Frances Brookey, Principal Analytical Investigator Morse Laboratories, Inc. 1525 Fulton Avenue Sacramento, CA 95825
Study Director and Author:	Tami I. Belcher Excel Research Services, Inc. 3021 W. Dakota Ave., Suite 110 Fresno, CA 93722
Report Date:	March 14, 2001
Identifying Codes:	MRID # 453592-01 and 454009-01 amended; Atochem Study Number KP-2000-03; Excel Study Number ERS2003

EXECUTIVE SUMMARY

This report reviews a dislodgeable foliar residue (DFR) and soil residue dissipation (SRD) study submitted by Cerexagri, Inc. (formerly Elf Atochem North America, Inc.) in response to the EPA Agricultural Reentry Data Call-In issued on October 18, 1995 and amended January 1997. The insecticide methyl parathion was applied to walnuts in three geographical locations in southern California. The study was conducted in California only, because Penncap-M® has a Section 24(c), Special Local Needs label and is used to control codling moth, navel orange worm, San Jose scale, and walnut scale and almost 100 percent of commerical walnuts are grown in California. Penncap-M®, a flowable formulation consisting of a water suspension of polymeric-type microcapsules which contain 20.9 percent methyl parathion, was applied at all locations. This study was conducted to determine the residue levels of methyl parathion and its oxygen analog, methyl paraoxon, that can be dislodged from walnut foliage and soil following four applications of the test substance, each at the maximum application rate of 2 pounds ai per acre. All applications were made using ground airblast application equipment.

Walnut leaf punch samples were collected from treated and untreated control plots in Fresno, Ripon, and Porterville, three walnut growing regions of California. Sampling was performed immediately prior to and after each of the four applications, 8 and 24 hours after the fourth application, and 2, 3, 5, 7, 10 (11 in Porterville), 14 (15 in Porterville), 21 (20 in Fresno), 28, 35, and 42 (40 in Porterville) days after the fourth treatment. Soil dust samples were also collected at the three test sites at the following intervals: immediately prior to and after each of the four applications, 8 and 24 hours after the fourth application, and 5 (Ripon site only), 7, 10 (11 in Porterville), 14 (15 in Porterville), 21 (20 in Fresno), 28, and 35 days after the fourth application.

The maximum average dislodgeable foliar methyl parathion residues occurred immediately after the fourth application in Fresno and Ripon, and immediately after the first application in Porterville. Average residue levels after the fourth application were: (1) Fresno - 2.89 $\mu g/cm^2$; (2) Ripon - 2.76 $\mu g/cm^2$; and (3) Porterville - 0.947 $\mu g/cm^2$. Residue levels did not decline below the LOQ (0.01 or 0.001 $\mu g/cm^2$) at any of the sites. Methyl paraoxon residue levels were much lower than methyl parathion residue levels. Average methyl paraoxon residue levels after the fourth application were all below the LOQ (0.01 $\mu g/cm^2$). Residue levels remained below the LOQ (0.01 $\mu g/cm^2$) throughout the sampling period at Ripon, but were intermittently detected above the LOQ (0.01 or 0.001 $\mu g/cm^2$) at various sampling intervals at the other two test sites.

The maximum average dislodgeable soil methyl parathion residues occurred immediately after the third application in Fresno (341 $\mu g/g$), the first application in Ripon (165 $\mu g/g$), and the fourth application in Porterville (91.8 $\mu g/g$). Residues were corrected for moisture content. Average methyl parathion residue values after the fourth application were 65.8 $\mu g/g$ (Fresno), 21.6 $\mu g/g$ (Ripon), and 91.8 $\mu g/g$ (Fresno). The average residue values varied significantly from site to site following each application. Residue values did not decline below the LOQ at any of the sites. Methyl paraoxon residue levels were much lower than methyl parathion residue levels.

Average methyl paraoxon residue levels after the fourth application were all below the LOQ (0.5 μg/g). Residue levels remained below the LOQ (0.5 or 0.05 μg/g) throughout the sampling period at Fresno and Ripon, but were detected 8 hours after the fourth applicaton in Porterville (0.875 μg/g) before they declined below the LOQ. The maximum average methyl paraoxon residues occurred immediately prior to the third application in Fresno (3.09 μg/g), immediately after the second application in Ripon (2.73 μg/g), and 8 hours after the fourth applicaton in Porterville (0.875 μg/g).

The study author transformed DFR residues to $\mu g/cm^2$ by dividing the actual residues by 400 cm^2/sample. SRD residues were transformed to residues per $\mu g/cm^3$ by multiplying the total μg/gram found by the total grams collected and then dividing the total μg found by the total cm^3 of soil collected. Residues were not corrected for moisture content. Averages were calculated using residue values measured as less than the LOQ as equal to the LOQ. The data were corrected using the overall field fortification recoveries for each analyte from the respective field sites. Data were only corrected when the recoveries were less than or equal to 100 percent and the residues were greater than the LOQ.

Linear regression analyses were performed by the study author on the average methyl parathion DFR ($\mu g/cm^2$) and SRD data ($\mu g/cm^3$). Analyses were not performed for methyl paraoxon residues due to their intermittent detection. First-order kinetics were used to predict the residue half-lives. Micorsoft's® Excel 2000 linear regression function was applied to the log (ln) transformed data. Methyl parathion residues from samples collected immediately after the fourth application through the last day of sampling were included.

The study author calculated dissipation half-lives and correlation coefficients for methyl parathion residues as follows:

DFR Residues - Methyl Parathion

- Fresno 7.76 days ($r^2 = 0.80$)
- Ripon 5.41 days ($r^2 = 0.80$)
- Porterville 6.28 days ($r^2 = 0.83$)

SRD Residues - Methyl Parathion

- Fresno 13.50 days ($r^2 = 0.57$)
- Ripon 8.76 days ($r^2 = 0.81$)
- Porterville 8.14 days ($r^2 = 0.68$)

Versar also used average DFR and SRD values in conducting linear regressions for the three test sites. The regressions were performed using the total residue level in each sample (sum of methyl parathion and methyl paraoxon), since methyl parathion and methyl paraoxon are assumed to have the same toxicity. If a residue level was less than the LOQ, then a value one-half of the LOQ was used to calculate the sum of total residues in selected samples. DFR and SRD values beginning with the samples collected immediately after the fourth application through the last day of sampling were included. Data reported as total μg of analyte per gram of soil (corrected for soil moisture) were used in the SRD regressions.

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

DFR Residues - Total Residue

- Fresno 7.78 days ($r^2 = 0.80$)
- Ripon 5.41 days ($r^2 = 0.80$)
- Porterville 6.46 days ($r^2 = 0.84$)

SRD Residues - Total Residue

- Fresno 5.41 days ($r^2 = 0.88$)
- Ripon 8.21 days ($r^2 = 0.81$)
- Porterville 4.41 days ($r^2 = 0.87$)

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

- The product label states that the minimum spray interval is 21 days. At the Ripon test site, the interval between the second and third applications was 29 days due to wet soil conditions and excessive wind.

- The overall field fortification recovery for DFR samples of methyl paraoxon from Ripon (66 ± 48 percent) showed a high degree of scatter. The study author stated that the reason for the scatter is unknown, however, it is possible that field fortification techniques may have been a contributing factor, as indicated in the field raw data for this site.

- Information on study validation was not provided. The study report states that the method used to analyze DFR samples was validated; however, information was not provided. The method used to analyze SRD samples is dated November 8 and November 29, 2000, after the current study was initiated (August 14, 2000).

- The analytical method used for the analysis of SRD samples has a target LOQ of 0.05 ppm for each analyte. The Study Protocol indicated an LOQ of 0.01 ppm which was not achievable. For some samples the LOQ was adjusted to 0.5 ppm.

- Rainfall occurred on 2nd and 14th day after the fourth application in Ripon, and on 7th and 10th day after the fourth application in Porterville.

- At the Ripon test site, leaf punch samples could not be collected after the 21st day after the fourth application because of premature leaf loss.

STUDY REVIEW

Study Background

This report reviews a dislodgeable foliar residue (DFR) and soil residue dissipation (SRD) study in walnuts submitted by Cerexagri, Inc. (formerly Elf Atochem North America, Inc.) in response to the EPA Agricultural Reentry Data Call-In issued on October 18, 1995 and amended January 1997. 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 including nuts. The study was conducted in California only, because Penncap-M® has a Section 24(c), Special Local Needs label and is used to control codling moth, navel orange worm, San Jose scale, and walnut scale and almost 100 percent of commerical walnuts are grown in California. The objective of this study was to determine the residue levels of methyl parathion and its oxygen analog, methyl paraoxon (CAS No. 950-35-6), that can be dislodged from walnut foliage and soil following four foliar applications of the test substance, each at a maximum application rate of 2 pounds ai per acre. All applications were made using ground airblast application equipment.

The field portion of the study was conducted at three geographical locations in Southern California. All field and analytical operations were overseen by Excel Research Services, Inc. of Fresno, California. On-site field operations were conducted by Excel Research Services, Inc. of Fresno, California; Plant Sciences, Inc. of Manteca, California; and Research For Hire of Porterville, California. All leaf and soil dust samples were analyzed by Morse Laboratories, Inc. of Sacramento, California. All DFR samples were stored frozen for a period ranging from 6 to 145 days; SRD samples were stored frozen for a period ranging from 7 to 133 days.

Test Plots

The test sites were located in Fresno (Fresno County), Ripon (San Joaquin County), and Porterville (Tulare County), three walnut growing regions of California. A companion walnut harvesting worker reentry study (KP-2000-06) was conducted concurrently at the Fresno and Porterville test sites (only the DFR and SRD studies are discussed in this review). The sites were selected to "represent the climatic and walnut-growing conditions expected in the intended-use areas." In 1997, California produced 269 tons of walnuts, 100 percent of the total U.S. walnut production (USDA).

A single treated and a single untreated (control) plot were established at each test site. The plots were maintained under typical cultural and irrigation practices. The walnut varieties tested in this study were suited to the geographical region in which they were grown. Varieties used were Frankette in Fresno and Porterville, and Hartley in Ripon. The approximate ages of the trees were 50 years (Fresno), 44 years (Porterville), and 8 years (Ripon). Soil types found at each site were Sandy Loam (Fresno and Ripon), and Loam (Porterville). The percent moisture at 1/3 bar/15 bar was 10.2/3.4 (Fresno), 11.5/NA (Ripon), and 22.1/8.7 (Porterville).

The overall treated test site at Fresno consisted of 7.86 acres to accommodate the DFR/SRD plot and the walnut harvesting reentry plot. The treated plot was 5 rows by 7 trees (tree spacing 40 feet, row spacing 40 feet) and measured 56,000 ft^2 (200 x 280 feet). The treated plot was divided into three replicates. Rows 1 and 5 were buffer rows and were not sampled. The control plot was 1 row by 5 trees (tree spacing 50 feet, row spacing 40 feet) and measured 8,000 ft^2 (200 x 40 feet). The control plot was located 175 feet upwind of the treated plot. The test site had a less than 2 percent slope. (Sample plot diagrams are provided on page 71 of the Study Report).

The treated plot at the Ripon site was 5 rows by 7 trees and measured 16,100 ft^2 (100 x 161 feet). The treated plot was divided into three replicates. Rows 1 and 5 were buffer rows and were not sampled. The control plot was 1 row by 5 trees and measured 2,400 ft^2 (20 x120 feet). The tree spacing was 23 feet and the row spacing was 20 feet for both plots. The control plot was located approximately 295 feet upwind of the treated plot. The test site had an estimated slope of less than 1 percent. (Sample plot diagrams are provided on page 72 of the Study Report).

The overall treated test site in Porterville consisted of 9.37 acres to accommodate the DFR/SRD plot and the walnut harvesting reentry plot. The treated plot was 5 rows by 7 trees and measured 65,800 ft^2 (280 x 235 feet). The treated plot was divided into three replicates. Rows 1 and 5 were buffer rows and were not sampled. The control plot was 1 row by 5 trees and measured 9,400 ft^2 (200 x 47 feet). The tree spacing was 40 feet and the row spacing was 47 feet for both plots. The control plot was located downwind; but more than 2000 feet from the treated plot. The test site had an estimated slope of 0.5 percent. (Sample plot diagrams are provided on page 73 of the Study Report).

For the SRD samples, the ground beneath the five designated trees per replicate were divided into 120 subplots, each measuring approximately 2 x 3 feet. Six predetermined subplots were sampled per replicate at each sampling event.

Field and Pesticide Use History

Walnuts were grown on all three tests sites for the three years (1997-1999) prior to the current study. In 1999, at the Fresno test site, two herbicides (Valor WDG® and Roundup

Ultra®) were applied to the test sites. Prior to the current study in 2000, Roundup Ultra® was applied monthly from February to July (except April). No pesticides were applied in 1997 or 1998. A complete listing of the pesticides and their rate of application is provided on page 240 of the Study Report. During the course of the current study, Roundup Ultra® was applied twice, to the berms only, at the rate of 1 pound ai per acre to control weeds.

The test site in Ripon received 25 applications of 12 pesticides in 1998 and 1999. The pesticides applied included nine herbicides, one fungicide, and two organophosphate insecticides (Lorsban 4E® and Imidan 70WP®). A complete listing of the pesticides and their rate of applications is provided on page 252 of the Study Report. Prior to the current study, two fungicides, two herbicides, and one organophosphate insecticide were applied to the test site between February and July 18, 2000. The organophosphate insecticide (Lorsban 4E®) was applied once at the rate of 2 pounds ai per acre, approximately 4 months prior to the initial application of the test substance. A complete listing of the pesticides and their rate of applications is provided on page 256 of the Study Report. Information on the pesticides applied in 1997 was not available (a deviation from the Study Protocol). No pesticide maintenance chemicals were applied during the course of the current study.

No maintenance chemicals were applied to the Porterville test site for the three years prior to the current study (1997-2000). During the course of the current study, a herbicide was applied once (Gramoxone Extra®) at the rate of 0.8 pounds ai per acre to control weeds.

Materials and Application

A Special Local Needs label for Penncap-M® (EPA Reg. No. 4581-393 and EPA SLN No. CA-000001) 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 per gallon. In California, it can be applied to walnuts using ground or aerial equipment, and a sufficient water volume for thorough coverage. For aerial applications, a minimum of 10 gallons per acre total spray volume should be used. The total spray volume should be increased depending on the size of the trees being treated. The maximum application rate for walnuts is 8 pints of formulated product per acre or 2.0 pounds ai per acre. Applications should not be made within 14 days of harvest. The minimum spray interval is 21 days and the maximum application is 32 pints per season, including dormant and post-harvest applications.

In this study, walnuts grown at each test site were sprayed four times with Penncap-M® at the maximum label rate of 2.0 pounds ai per acre per application. The four applications were made using ground airblast application equipment calibrated to deliver approximately 100 to 200 gallons per acre spray volume. The four applications were made at a 21-day interval, with one exception. At the Ripon test site, the interval between the second and third applications was 29 days due to wet soil conditions from rainfall and excessive winds. Actual application rates were within ± 4 percent (7.7 to 8.1 pints per acre) of the target for all applications at all sites. The equipment was calibrated based on the total output from the sprayer measured in duplicate or triplicate over 30 seconds. The average output was calculated and the speed was determined based on the desired output in gallons per acre.

The four applications at the Fresno site were made using a tractor-mounted Rears airblast sprayer equipped with a 150-gallon tank with paddle agitation. The sprayer was equipped with 10 TeeJet D6 and D7 nozzles with No. 46 swirl plates operating at approximately 200 psi. The actual spray volume was 100-101 gallons per acre. At the time of the applications, the growth stage varied from nut sizing at the initial application to mature by the fourth application.

The four applications at the Ripon site were made using a tractor-mounted Air-O-Fan SR-II32 airblast sprayer equipped with a PTO driven pump. The sprayer was equipped with 7 TeeJet D4 nozzles with No. 33 swirl plates operating at approximately 200 psi. The actual spray volume was 145-151 gallons per acre. The west side of the first three trees in the outer row were sprayed twice at the second application due to tractor operator error. No adverse impact on the study was anticipated since the double spray occurred in an outer nonsampled row and was directed outward. At the time of the applications, the growth stage varied from kernel growth at the initial application to post maturity (leaf drop) at the fourth application.

The four applications at the Porterville site were made using a tractor-mounted Air-O-Fan Airblast GB36 sprayer equipped with a PTO pump. Mechanical agitation was used for each application. The sprayer was equipped with 10 TeeJet D7 and D8 nozzles with 4-hole cores operating at 110 to 120 psi. The actual spray volume was 120-124 gallons per acre. At the time of the applications, the growth stage varied from nut sizing at the initial application to near maturity by the fourth application.

Meteorology

The statement of GLP Compliance prepared for the study states that weather data (current and/or historical) were not collected per the GLP regulations. Air temperature readings, relative humidity readings, wind speed and direction, cloud cover, and soil temperature and moisture readings were presented in the report for the days of application at each test site. Hand-held instruments were used to collect the data. Daily/monthly precipitation and air temperature data were provided for the period of applications and sampling. Average 10-year (1990-1999) or 30-year (1961-1990) historical meteorological data (monthly air temperature and precipitation) were also provided. The report states that there were "not significant departures from normal air temperatures during the trial period." However, rainfall was above normal in October and below normal for November and December at all three test sites. This did not appear to adversely impact walnut growth or vigor at the Fresno and Porterville sites, but may have been a contributing factor for the premature leaf loss at the Ripon site.

At the Fresno site, precipitation data were collected from a rain gauge placed near the treated plot. Other current weather data were collected from Excel's Weather Station No. 1, located approximately 20 miles northwest of the test site. Historical data were collected from the

NOAA Fresno weather station located approximately 14 miles southeast of the test site. A total of 3.30 inches of rain fell after the initial application of the test substance (see page 243 in the Study Report). All of the rainfall occurred during the third month of the study period (October), with the first days of rainfall occurring 9-11 days before the fourth application (1.70 inches). All of the other rainfall occurred 6 and 9 days after the fourth application. A total of 1.6 inches of rain fell from the fourth application to the last day of sampling. No rain fell on any sampling days. The average (monthly) minimum air temperatures during the course of the study ranged from 59°F in August to 36°F in December; average maximum air temperatures ranged from 93°F to 57°F. Climatic conditions reported at the time of the applications show air temperatures ranging from 79°F to 92°F, relative humidity readings of 22 to 52 percent, dry surface soils, and winds 0-3 mph. No supplemental irrigation was used after the test applications and sampling began.

At the Ripon site, precipitation data were collected from a rain gauge located at the Plant Sciences, Inc. Manteca facility located approximately 2 miles northwest of the trial site (a deviation from the Study Protocol, but no adverse effect is anticipated by the study author). Other current and historical weather data were collected from the CIMIS Weather Station No. 70 located approximately 6 miles northwest of the test site. A total of 3.45 inches of rain fell after the initial application of the test substance (see page 255 in the Study Report). This rainfall occurred during the months of October (2.86 inches), November (0.25 inches), and December (0.34 inches). The first days of rainfall occurred over the 3 days following the second application of the test substance (0.65 inches). Rain also fell on two sampling days: the 2nd (0.10 inches) and the 14th (0.15 inches) day after the fourth application. A total of 0.44 inches of rain fell from the fourth application to the last day of sampling. The average (monthly) minimum air temperatures, during the course of the study, ranged from 53°F in September to 31°F in January; average maximum air temperatures ranged from 85°F to 57°F (December). Climatic conditions reported at the time of the applications show air temperatures ranging from 49°F to 85°F, relative humidity readings of 47 to 100 percent, dry to moist surface soils, and winds 0-5 mph. No supplemental irrigation was used after the test applications and sampling began.

At the Porterville site, precipitation data were collected from an on-site Tru-chek rain gauge. Other current weather data were collected from the Research For Hire weather station located 6.5 miles south of the test site. Historical data were collected from the NOAA weather station located in Porterville, approximately 3.5 miles southeast of the test site. Rainfall was much less (50 percent) at the Porterville test site than at Fresno and Ripon. A total of 1.57 inches of rain fell after the initial application of the test substance; all in the month of October (see page 268 in the Study Report). The first three days of rainfall occurred 7-9 days prior to the fourth application (0.74 inches). Another 0.14 inches of rain fell 7 days after the fourth application (0.14 inches) and was followed by 0.52 inches of rain 10 days after the fourth application. A total of 0.76 inches of rain fell from the fourth application to the last day of sampling. The average (monthly) minimum air temperatures during the course of the study ranged from 61°F in August to 35°F in November; average maximum air temperatures ranged from 94°F to 60°F. Climatic conditions reported at the time of the applications show air temperatures ranging from

68°F to 88°F, relative humidity readings of 38 to 62 percent, dry to moist surface soils, and winds 0-1.5 mph. Supplemental irrigation was applied to the test plots by microsprinkler four times during the course of the study. A total of 2.0 inches was applied in August, 3.5 inches in September, and 1.5 inches in October. Irrigation amounts were estimated by the grower.

Sampling of Leaf and Soil Dislodgeable Residue Samples

Leaf Punch Samples

Walnut leaf punch samples were collected (or scheduled to be collected) at the three test sites at the following intervals: immediately prior to and after each of the four applications, 8 and 24 hours after the fourth application, and 2, 3, 5, 7, 10, 14, 21, 28, 35, and 42 days after the fourth treatment. Samples were collected as scheduled with the following exceptions. The 10, 14, and 42 days after the fourth application samples for the Porterville test site were actually collected 11, 15, and 40 days after the fourth treatment because of rainfall, harvest reentry schedule, and anticipated rainfall, respectively. The samples for the Fresno site were actually collected on the 20th day after the fourth application. In addition, DFR samples were not collected at the Ripon site 28, 35, and 42 days after the fourth application because of premature leaf loss due to climatic conditions.

At each sampling interval, a single leaf punch sample was collected from the untreated control plot and triplicate samples were collected (one from each replicate) from the treated plot. Each sample consisted of 40 leaf discs. Attempts were made to collect leaf discs from all areas of the trees and from all four quadrants. Most of the leaf discs were collected from the low to mid portions of the trees since sampling the top of the 50 foot trees was not possible without disturbing potential residue from the lower sections. (The report states no adverse impact is anticipated, see Protocol Deviation No. 19, page 196.) Exceptions occurred at the Ripon test site due to premature leaf loss, which resulted in not all trees being sampled at each interval, more or less than eight leaf discs being collected from each tree, and not all of the quadrants being sampled. (The report states minimal impact is anticipated since a residue dissipation curve can still be prepared. See Protocol Deviation No. 18, page 195.) Field fortification samples were prepared immediately after the second application (Fresno and Ripon sites only), the third application (Porterville site only), the fourth application, and on 14th day after the fourth application (Fresno and Porterville sites only). Fortification samples were collected in the same manner as the field collected samples. Samples were prepared after the third application in Porterville because an adequate supply of the methyl paraoxon analytical standard was not available at the time of the second application. In addition, the 14th day after the fourth application fortification event was postponed one day to coincide with the harvesting reentry event.

Samples consisted of a 405 cm^2 leaf surface area, counting both sides of the leaf surface. A Birkestrand leaf punch with a 1.0 inch diameter was used to collect 40 discs per sample. Separate leaf punches were used for the untreated and treated plots. The untreated samples were collected prior to the treated samples to minimize cross-contamination. All leaf punch samples were collected when the foliage was dry, with the exception of the 24-hour, and postapplication #4 samples at Ripon where the leaves were wet from dew and rain. (The report states that no adverse effect is anticipated. See Protocol Deviation No. 28, page 205.) Leaf disc samples were transported and held in coolers with substitute ice until dislodging. (Exceptions occurred at the postapplication 4 and 8 hour sampling events in Ripon. No adverse effect is anticipated by the study author since outdoor conditions were cool (48 °F - 50 °F) and samples were dislodged within 3 hours. See Protocol Deviation No. 27, page 204). The dislodging procedure generally began within four hours of collection (exceptions are not noted in the Study Report) and was conducted at the field laboratories. Leaf disc samples were dislodged two times with 100 mL of a 0.01 percent Aerosol OT 75 solution. Samples were placed on a reciprocal shaker for approximately 10 minutes and then decanted into a glass jar. After dislodging, the samples were immediately placed into freezer storage. Details on the sampling dislodging procedures are available in the Study Report.

Soil Dust Samples

Soil dust samples were collected at the three test sites at the following intervals: immediately prior to and after each of the four applications, 8 and 24 hours after application the fourth application, and 5 (Ripon site only), 7, 10 (11 in Porterville), 14 (15 in Porterville), 21 (20 in Fresno) and 35 days after the fourth application. Soil samples were not collected prior to the third application at the Porterville site due to wet soil conditions from irrigation.

At each sampling event, triplicate soil dust samples were collected from the treated plot and a single sample was collected from the untreated control plot. Samples were collected using a Dirt Devil® hand-held vacuum or scooping method, depending on the conditions of the soil surface. The hand-held vacuum was used if the soil was dry and the scooping method was used when the soil was either too wet or could not otherwise be collected by the vacuum. Most of the samples in this study were collected using the scoop method (Amendment No. 5) due to moist soil conditions from rain/fog. The Study Report states that "with this method of soil collection, there is a tendency for higher variance and it is possible that the actual residues available for respiration may be exaggerated." A 100-mesh brass screen was used to select the required, filtered dust particles 147 microns in size or smaller. The soil surface area per sample was approximately 2,700 cm^3, based on the soil sampling frame (18 cm x 25 cm x 1 cm). A total of six subplots was subsampled and composited into one sample per replicate. A minimum of 50g of soil was required per sample. (Four samples collected at the pre-and postapplication #1 events in Ripon weighed less than 50 grams due to moist soil conditions. The study author anticipates no adverse effects. See Protocol Deviation #25, page 202). Soil samples, regardless of sampling method used, were transferred into prelabeled glass jars with Teflon®-lined caps. Samples were transported to freezer storage until shipment to the analytical laboratory.

Field fortification samples were prepared immediately after the second application (Fresno and Ripon sites only), the third application (Porterville site only), the fourth application, and on the 14th day after the fourth application. Fortification samples were collected in the same manner as the field collected samples. Triplicate samples were fortified at each event. Samples were immediately placed into freezer storage after fortification. The samples were transferred to the analytical laboratory for analysis following the same procedures as the actual field samples for this study.

QA/QC

Sample Handling and Storage

Applications of the test substance at the Fresno site were made on August 18, September 8, September 29, and October 20, 2000. Samples were collected between August 17 and December 1, 2000. In Ripon, applications of the test substance were made on September 18, October 9, November 7, and November 28, 2000. Samples were collected between September 18, 2000 and January 2, 2001. In Porterville, applications of the test substance were made on August 17, September 7, September 28, and October 19, 2000. Samples were collected between August 16 and November 28, 2000.

At the field facilities, leaf punch samples were dislodged with 0.01 percent Aerosol® OT. After dislodging, the dislodging solution samples were placed into freezer storage within 45 minutes of dislodging. Soil samples were transferred directly to the freezers within 4 hours of collection. Samples were stored frozen at temperatures between -18°F and 23°F.

All samples were shipped from the test sites within 1 to 27 days of sample collection. Samples were either hand-delivered or shipped frozen to the analytical laboratory, Morse Laboratories, in Sacramento, California, on dry ice via Federal Express overnight service or by ACDS freezer truck service. All samples were labeled in the field with the study number, sample number, and sample type.

Upon arrival at Morse Laboratories, the samples were transferred to a freezer for storage where they remained until thawed for analysis. All DFR samples were extracted between 6 and 145 days and SRD samples between 7 and 133 days of collection. Freezer storage samples were maintained at -20 ± 5°C.

Product and Tank Mix Analysis

Prior to study initiation, the sponsor made determinations of purity, strength, stability, and composition of the formulation. The substance was assayed at 20.2 percent ai with an expiration date of June 23, 2001. Tank mix analyses were not performed.

Analytical Methodology

DFR Samples

Morse Laboratories, Inc. analyzed samples of Aerosol® OT dislodging solution, used to surface extract walnut foliage, in order to determine dislodgeable residues of methyl parathion and methyl paraoxon. Field fortification samples, as well as laboratory (procedural) fortification samples, were also analyzed. The analytical method used was identified as: Morse Laboratories, Inc. Analytical Method No. Meth-121, Revision No. 3, dated May 12, 2000, entitled, "Determination of Methyl Parathion and its Oxygen Analog in Dislodgeable Foliar (DFR) Solutions." Modifications to the method, dated September 8, 2000 and October 4, 2000, were used to lower the LOQ from 0.01 $\mu g/cm^2$ to 0.001 $\mu g/cm^2$. The modified method was used on selected samples during the course of the study. Copies of these documents are presented in Appendix I and II of the Study Report. The Study Report states that the method was validated by Morse Laboratories; however, information on a validation study is not provided in this Study Report.

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 NaC1 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 and Hewlet-Packard 6890 gas chromatographs employing flame photometric detection (FPD) in the phosphorus mode. The typical run time was approximately 10 minutes and the typical retentions times were approximately 4.8 and 5.0 minutes for methyl parathion and methyl paraoxon, respectively. A complete listing of typical instrument conditions is provided in the Study 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 Study Report. Chromatograms show good peak separation and sharpness of peaks.

Revisions to *Analytical Method-121* are reported in "Modifications to Analytical Method No. Meth-121: September 8, 2000 and October 4, 2000." The method was modified to permit residue determination at a lower LOQ of 0.001 $\mu g/cm^2$ on selected samples. Modifications are noted on page 307 of the Study Report.

SRD Samples

Morse Laboratories, Inc. analyzed soil samples to determine dislodgeable residues of methyl parathion and methyl paraoxon. Field fortification samples, as well as laboratory (procedural) fortification samples, were also analyzed. The analytical method used was identified as: Morse Laboratories, Inc. Analytical Method-122, Revisions No. 2 and No. 3, dated November 8, 2000 and November 27, 2000, entitled, "Determination of Methyl Parathion and its Oxygen Analog in Topsoil Dust." Copies of these documents are provided in Appendix III of the Study Report. Information on a validation study was not provided.

Analytical Method-122 was used for the analysis of methyl parathion and methyl paraoxon in SRD solutions. For SRD samples containing moisture (collected using the scoop method), water was added to all samples regardless of moisture content. Tetrahydrofuran (THF) was added and the sample was extracted with the THF/water mixture. The water was salted out and an aliquot of the THF phase was removed and purified by means of a carbon black SPE tube cleanup. The resulting purified extract was concentrated, then submitted to analysis.

For dry (dust) SRD samples (collected using a hand-held vacuum), the SPE was also utilized. THF was added to the sample and the resulting dust suspension, mixed with Celite, was placed on top of a laboratory prepared (or Supelco customized) solid phase extraction (SPE) tube containing two sorbents (Florisil® on the bottom, followed by ENVI®-Carb). The analytes were eluted from the column with 50 percent toluene/50 percent acetone (v/v) and further purified using silica SPE cleanup. The resulting purified extract was concentrated, then submitted to GC analysis. The SRD samples analysis employed the same instrumentation conditions as described for the DFR samples (see previous section).

Percent moisture was determined for the SRD samples and was used to adjust the residue levels reported for both methyl parathion and methyl paraoxon. The analytical method used for moisture determination was Morse Laboratories, Inc. SOP No. Pest-17a, Revision No. 6, dated November 17, 2000, entitled, "Analysis of Percent Moisture and the Determination of Constant Weight." An SOP deviation was generated to reduce the drying time of dry SRD samples from 2 hours to 1 hour. Both documents are provided in Appendix IV of the Study Report.

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

The analytical method used for the analysis of DFR samples had a limit of quantitation (LOQ) of 0.01 $\mu g/cm^2$ for both methyl parathion and methyl paraoxon. Select DFR samples were analyzed using a modified version of the method which permitted determination of the analytes down to an LOQ of 0.001 $\mu g/cm^2$. The level of detection (LOD) was not defined in the Study Report. An earlier study completed by the registrants, reported LODs of 0.003 $\mu g/cm^2$ and 0.0003 $\mu g/cm^2$ for the same methods.

The analytical method used for the analysis of SRD samples had a target LOQ of 0.05 ppm (μg/g) for each analyte. (The Study Protocol indicated an LOQ of 0.01 ppm which was not achievable. No adverse effect is anticipated by the study author.) In samples where methyl parathion residues were in excess of 10 ppm (on a dry weight basis), there was inadequate separation between methyl parathion and methyl paraoxon GC responses, thus impacting the LOQ for methyl paraoxon. In these cases, the LOQ of 0.05 ppm for methyl paraoxon could not be achieved. Therefore, the LOQ for methyl paraoxon was adjusted to 0.5 ppm when methyl parathion residues exceeded 10 ppm. For samples containing less than 10 ppm methyl parathion residues, the LOQ for methyl paraoxon remained at 0.05 ppm. The level of detection (LOD) was not defined.

Laboratory Recovery

Procedural recovery of methyl parathion and methyl paraoxon was evaluated at two fortification levels for each analytical set. The laboratory fortification levels were selected to bracket the anticipated residues detected on the field samples. Control samples were fortified at levels ranging from 0.001 μg/cm^2 to 4000 μg/cm^2 for DFR samples and from 0.05 ppm to 200 ppm for SRD samples, and extracted concurrently with the field samples.

The overall average recovery for concurrent laboratory fortification DFR samples was 87 ± 9.5 percent (n=80) for methyl parathion and 93 ± 10 percent (n=70) for methyl paraoxon for routine DFR samples (LOQ of 0.01 μg/cm^2). The overall average recovery for DFR samples for the modified analyses was 92 ± 14 percent (n=12) for methyl parathion and 95 ± 9.9 percent (n=12) for methyl paraoxon.

The overall average recovery for concurrent laboratory fortification dry SRD samples was 103 ± 11 percent (n=44) for methyl parathion and 89 ± 11 percent (n=44) for methyl paraoxon. The overall average recovery for wet SRD samples was 99 ± 7.7 percent (n=43) for methyl parathion and 94 ± 12 percent (n=43) for methyl paraoxon.

All of the average procedural fortification recoveries were within the acceptable range of 70 to 120 percent. Individual laboratory fortification results are presented in Appendix V of the Study Report.

Field Fortification Recovery

Field fortification samples were prepared for each matrix (DFR and SRD) using methyl parathion and methyl paraoxon. The samples were prepared immediately after the second application (Fresno and Ripon sites only), third application (Porterville site only), fourth application, and on the 14th day after the fourth application (day 15 in Porterville). Only soil samples were fortified at the Ripon site on the 14th day after the fourth application. Triplicate control samples for each matrix and analyte were fortified at each event. Dislodging solutions were fortified separately with methyl parathion and methyl paraoxon at 4, 400, 2000, and 4000

(Fresno site only) μg/sample (0.01, 1.0, 5.0 and 10.0 $\mu g/cm^2$). Soil samples were fortified separately with methyl parathion and methyl paraoxon at 0.05, 0.5, and 100 ppm/sample. The fortified samples were stored frozen and handled in the same manner as the field samples.

Table 1 summarizes the overall average field fortified sample recovery rates. All reported field fortification recoveries for DFR and SRD samples were corrected for the mean recovery of concurrently analyzed freshly-fortified laboratory control samples. The overall average corrected field fortification recoveries for DFR samples of methyl parathion were 100 ± 9.7 percent, 101 ± 14 percent, and 110 ± 17 percent for the Fresno, Ripon, and Porterville sites, respectively. Methyl paraoxon DFR field fortification recoveries were 90 ± 12 percent for the Fresno site and 103 ± 9.2 percent for the Porterville site. The overall average recovery from the Ripon site (66 ± 48) was lower than guidelines (i.e., 90 percent), indicating correction of DFR field data is appropriate. In addition, the data showed a high degree of scatter. The study author states that the field fortification technique may have been a contributing factor, as indicated in the raw field data for this site. The stability of methyl parathion and methyl paraoxon in DFR solution was demonstrated in the field fortification samples based on the remainder of the results.

The overall average corrected field fortification recoveries results for SRD samples of methyl parathion were 96 ± 10 percent at the Fresno site and 95 ± 11 percent at the Porterville site. The overall average recovery from the Ripon site was 83 ± 14 percent, indicating that correction of the SRD field data is appropriate. The average methyl paraoxon SRD field fortification recoveries indicate that methyl paraoxon was not as stable (or possibly extractable) as methyl parathion. The average field fortification recoveries were 79 ± 12 percent, 79 ± 13 percent, and 64 ± 16 percent at the Fresno, Ripon, and Porterville sites, respectively. These data indicate that correction of the SRD field data is appropriate.

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

Analyte	Matrix	Fortification Level DFR - µg/sample (µg/cm²) SRD-ppm/sample	Fresno (percent)	Ripon (percent)	Porterville (percent)
Methyl Parathion	DFR	4.0 (0.01)	103 ± 11 (n=9)	115 ± 14 (n=6)	122 ± 16 (n=9)
		400 (1.0)	96 ± 7.8 (n=9)	97 ± 9.9 (n=6)	107 ± 18 (n=9)
		2000 (5.0)	105 ± 4.4 (n=3)	91 ± 8.1 (n=6)	100 ± 11 (n=9)
		4000 (10.0)**	97 ± 11 (n=6)	—	—
		Overall Average	**100 ± 9.7 (n=27)**	**101 ± 14 (n=18)**	**110 ± 17 (n=27)**
	SRD	0.05	103 ± 7.8 (n=9)	84 ± 12 (n=8)	98 ± 11 (n=9)
		0.5	90 ± 3.3 (n=9)	80 ± 14 (n=9)	93 ± 13 (n=9)
		100	94 ± 13 (n=9)	83 ± 17 (n=9)	94 ± 8.4 (n=9)
		Overall Average	**96 ± 10 (n=27)**	**83 ± 14 (n=26)**	**95 ± 11 (n=27)**
Methyl Paraoxon	DFR	4.0 (0.01)	93 ± 10 (n=9)	59 ± 55 (n=6)	103 ± 9.2 (n=9)
		400 (1.0)	84 ± 5.7 (n=2)	88 ± 0 (n=1)	—
		2000 (5.0)	82 ± 21 (n=2)	88 ± 0 (n=1)	—
		Overall Average	**90 ± 12 (n=13)**	**66 ± 48 (n=8)**	**103 ± 9.2 (n=9)**
	SRD	0.05	82 ± 9.8 (n=9)	79 ± 17 (n=9)	66 ± 10 (n=9)
		0.5	74 ± 8.2 (n=9)	76 ± 13 (n=9)	61 ± 11 (n=9)
		100	81 ± 15 (n=9)	81 ± 8.5 (n=9)	65 ± 25 (n=9)
		Overall Average	**79 ± 12 (n=27)**	**79 ± 13 (n=27)**	**64 ± 16 (n=27)**

* Corrected for average procedural (laboratory) recovery within the analytical set.
** Fortification prepared due to misunderstanding by the Analytical Principal Investigator.

Storage Stability Recovery

Storage stability data from a previously conducted study (Atochem Study No. KP-99-16 - Foliar Dislodgeable Residue Dissipation of Penncap-M® in Sweet Corn") indicated that methyl parathion and methyl paraoxon were stable in frozen DFR solution for up to 168 days. In that study, the average corrected recoveries were 100 percent for methyl parathion and 94.1 percent for methyl paraoxon. The maximum storage period for DFR samples collected in this study was 145 days.

The field fortified samples were used to indicate stability in SRD samples. The study author states that field fortification results indicate that methyl parathion was stable in SRD samples. However, the methyl paraoxon residues did not appear as stable (or possibly, as extractable) under the same storage and handling conditions. Since methyl paraoxon residues detected were insignificant when compared to methyl parathion, the study author states that the "overall effect of the total residue is considered negligible." The maximum storage period for SRD samples collected in this study was 133 days.

Results

Average methyl parathion and methyl paraoxon DFR and SRD sample residues are summarized in Tables 2 and 3. Averages were calculated using residue values measured as less than the LOQ as equal to the LOQ. The data were corrected using the overall field fortification recoveries for each analyte from the respective field sites (Table 1). Data were only corrected when the recoveries were less than or equal to 100 percent and the residues were greater than the LOQ. The LOQ was 0.01 $\mu g/cm^2$ for each analyte, however, select samples were analyzed using a modified version of the method which permitted determination of the analytes down to an LOQ of 0.001 $\mu g/cm^2$. No residues greater than the LOQ (0.01 $\mu g/cm^2$ or 0.001 $\mu g/cm^2$ for select samples) of either methyl parathion or methyl paraoxon were found in any untreated DFR samples. No residues greater than the LOQ (0.05 $\mu g/g$) of either methyl parathion or methyl paraoxon were found in any untreated SRD samples.

Since methyl parathion and methyl paraoxon are assumed to have the same toxicity, the total residue level in each sample was calculated as the sum of methyl parathion and methyl paraoxon. If a residue level was less than the LOQ, then a value of one-half the LOQ was used to calculate the sum of total residues in select samples, as noted.

Table 2. Average Methyl Parathion and Methyl Paraoxon DFR Sample Residues

Sampling Event	Fresno Site			Ripon Site			Porterville Site		
	Methyl Parathion[1] (μg/cm²)	Methyl Paraoxon[2] (μg/cm²)	Total Residue (μg/cm²)	Methyl Parathion[1] (μg/cm²)	Methyl Paraoxon (μg/cm²)	Total Residue (μg/cm²)	Methyl Parathion[1] (μg/cm²)	Methyl Paraoxon[1] (μg/cm²)	Total Residue (μg/cm²)
Pre-App 1	<0.001[3]	<0.001[3]	<0.001	<0.001[3]	<0.001[3]	<0.001	<0.001[3]	<0.001[3]	<0.001
Post-App 1	2.73	<0.01	2.74[8]	1.85	<0.01	1.86[8]	2.73	0.0114[4]	2.74
Pre-App 2	0.0870	<0.01	0.0870	0.205	<0.01	0.205	0.117	<0.01	0.117
Post-App 2	2.40	0.0118[4]	2.41	1.95	<0.01	1.96[8]	0.896	<0.01	0.901[8]
Pre-App 3*	0.408	<0.01	0.408	0.134	<0.01	0.134	0.111	<0.01	0.111
Post-App 3	2.85	0.0109[5]	2.86	2.34	<0.01	2.35[8]	1.38	<0.01	1.39[8]
Pre-App 4	0.222	<0.01	0.222	0.257	<0.01	0.257	0.0912	<0.01	0.912
Post-App 4	2.89	<0.01	2.90[8]	2.76	<0.01	2.77[8]	0.947	<0.01	0.952[8]
App 4, Hour 8	2.13	<0.01	2.14[8]	2.71	<0.01	2.71	1.71	0.0109[4]	1.72
App 4, Day 1	1.66	<0.01	1.67[8]	1.85	<0.01	1.85	0.966	0.0105[5]	0.977
App 4, Day 2	1.75	0.0184	1.77	0.939	<0.01	0.939	1.95	0.0169	1.97
App 4, Day 3	1.67	0.0212	1.69	1.11	<0.01	1.11	1.55	0.0175	1.57
App 4, Day 5	1.32	0.0265	1.35	0.492	<0.01	0.492	1.11	0.0141	1.12
App 4, Day 7	0.373	<0.01	0.378[8]	0.334	<0.01	0.334	0.466[3]	0.00507[3]	0.471
App 4, Day 10 (Day 11 in Porterville)	0.284	<0.01	0.289[8]	0.351	<0.01	0.351	0.241[3]	0.00208[3]	0.243

Table 2. Average Methyl Parathion and Methyl Paraoxon DFR Sample Residues (continued)

Sampling Event	Fresno Site			Ripon Site			Porterville Site		
	Methyl Parathion[1] (µg/cm²)	Methyl Paraoxon[2] (µg/cm²)	Total Residue (µg/cm²)	Methyl Parathion[1] (µg/cm²)	Methyl Paraoxon (µg/cm²)	Total Residue (µg/cm²)	Methyl Parathion[1] (µg/cm²)	Methyl Paraoxon[1] (µg/cm²)	Total Residue (µg/cm²)
App 4, Day 14 (Day 15 in Porterville)	0.314	<0.01	0.319[8]	0.348	<0.01	0.348	0.0580	<0.01	0.0630[8]
App 4, Day 21 (Day 20 in Fresno)	0.0600	<0.01	0.0650[8]	0.161	<0.01	0.161	0.141[3]	0.00105[3,7]	0.142
App 4, Day 28	0.139[3]	0.00161[3,6]	0.141	—	—	—	0.0186	<0.01	0.0236[8]
App 4, Day 35	0.0954[3]	0.00104[3,7]	0.0964	—	—	—	0.0334	<0.01	0.0384
App 4, Day 42 (Day 40 in Porterville)	0.0682[3]	<0.001[3]	0.0687[8]	—	—	—	0.0401[3]	0.00112[3,7]	0.0412

Footnotes:

1 Residues not corrected for average field fortification recoveries since recoveries were ≥ 100 percent.
2 Residues > LOQ corrected for average field fortification recoveries for the Fresno site (90 percent).
3 Samples analyzed with LOQ of 0.001 µg/cm².
4 One of three values <0.01 µg/cm², used 0.01 µg/cm² to calculate average. (method the study author used to calculate average residue)
5 Two of three values <0.01 µg/cm², used 0.01 µg/cm² to calculate average.
6 One of three values <0.001 µg/cm², used 0.001 µg/cm² to calculate average.
7 Two of three values <0.001 µg/cm², used 0.001 µg/cm² to calculate average.
8 Used ½ LOQ to calculate total residue.
* Interval between second and third application at the Ripon site extended to 29 days due to wet soil concentrations from rainfall.
– Samples not collected due to premature leaf loss.

NOTE: The LOQ was 0.01 µg/cm² for each analyte; however, selected samples were analyzed using a modified version of the method which permitted determination of the analytes down to an LOQ of 0.001 µg/cm².

Table 3. Average Methyl Parathion and Methyl Paraoxon SRD Sample Residues (μg/g dry weight)

Sampling Event	Fresno Site[1,2]			Ripon Site[1,2]			Porterville Site[1,2]		
	Methyl Parathion (μg/g)	Methyl Paraoxon (μg/g)	Total Residue (μg/g)	Methyl Parathion (μg/g)	Methyl Paraoxon (μg/g)	Total Residue (μg/g)	Methyl Parathion (μg/g)	Methyl Paraoxon (μg/g)	Total Residue (μg/g)
Pre-App 1	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Post-App 1	104	0.52[4]	104	165	0.588[4]	166	56.0	<0.5	56.3
Pre-App 2	2.52	0.130	2.65	25.0	2.49	27.5	0.315	0.0538[6]	0.369
Post-App 2	83.3	0.571[3]	83.9	226	2.73	129	37.7	<0.5	38.0[7]
Pre-App 3*	25.8	3.09	28.9	1.00	<0.05	1.03[7]	**	**	**
Post-App 3	341	2.62	344	2.30	<0.05	2.33[7]	19.1	0.841	19.9
Pre-App 4	4.88	0.161[5]	5.04	0.860	<0.05	0.885	0.364	<0.05	0.614[7]
App 4, Hour 0	65.8	<0.5	66.1[7]	21.6	<0.5	21.8[7]	91.8	<0.5	92.0[7]
App 4, Hour 8	51.0	<0.5	51.0	16.9	<0.5	16.9	35.1	0.875[3]	35.9
App 4, Day 1	66.5	<0.5	66.5	10.5	<0.05	10.5	18.9	<0.5	19.1[7]
App 4, Day 5 (Ripon only)	—	—	—	5.29	<0.05	5.29	—	—	—
App 4, Day 7	11.1	<0.05	11.1	3.79	<0.05	3.79	7.07	<0.05	7.07
App 4, Day 10 (Day 11 in Porterville)	5.70	<0.05	5.70	2.08	<0.05	2.08	1.66	<0.05	1.66
App 4, Day 14 (Day 15 in Porterville)	3.19	<0.05	3.19	2.08	<0.05	2.07	0.921	<0.05	0.921

Sampling Event	Fresno Site[1,2]			Ripon Site[1,2]			Porterville Site[1,2]		
	Methyl Parathion (μg/g)	Methyl Paraoxon (μg/g)	Total Residue (μg/g)	Methyl Parathion (μg/g)	Methyl Paraoxon (μg/g)	Total Residue (μg/g)	Methyl Parathion (μg/g)	Methyl Paraoxon (μg/g)	Total Residue (μg/g)
App 4, Day 21 (Day 20 in Fresno)	1.66	<0.05	1.66	1.42	<0.05	1.42	0.553	<0.05	0.553
App 4, Day 28	1.29	<0.05	1.29	0.901	<0.05	0.90	0.427	<0.05	0.427
App 4, Day 35	0.95	<0.05	0.95	1.03	<0.05	1.03	0.241	<0.05	0.241

Footnotes:

1 Total μg of analyte per gram of soil found (corrected for moisture content).

2 Residues > LOQ corrected for average field fortification recoveries for methyl parathion/methyl paraoxon (Fresno - 96%/79%; Ripon = 83%/79%; Porterville = 95%/64%).

3 One of three values <0.5 $\mu g/cm^2$, used 0.25 $\mu g/cm^2$ to calculate average.

4 Two of three values <0.5 $\mu g/cm^2$, used 0.25 $\mu g/cm^2$ to calculate average.

5 One of three values <0.05 $\mu g/cm^2$, used 0.025 $\mu g/cm^2$ to calculate average.

6 Two of three values <0.05 $\mu g/cm^2$, used 0.025 $\mu g/cm^2$ to calculate average.

7 Used ½ LOQ to calculate total residue.

* Interval between second and third application at the Ripon site extended to 29 days due to wet soil conditions from rainfall.

** Samples not collected due to wet soil conditions.

– Samples not collected.

μg/g = ppm

NOTE: The target LOQ for methyl parathion was 0.05 ppm. For samples containing methyl parathion residues >10 ppm, the LOQ for methyl paraoxon was 0.5 ppm. For samples containing methyl parathion residues <10 ppm, the LOQ was 0.05 ppm.

DFR Sample Residues

The maximum average dislodgeable foliar methyl parathion residues occurred immediately after the fourth application in Fresno and Ripon, and immediately after the first application in Porterville. Average residue levels after the fourth application were: (1) Fresno - 2.89 $\mu g/cm^2$; (2) Ripon - 2.76 $\mu g/cm^2$; and (3) Porterville - 0.947 $\mu g/cm^2$. Residue levels did not decline below the LOQ (0.01 or 0.001 $\mu g/cm^2$) at any of the sites. Residue levels on the last day of sampling (42 days after the fourth application in Fresno, 40 days after the fourth application in Porterville, and 21 days after the fourth application in Ripon) were 0.0682 $\mu g/cm^2$ (Fresno), 0.161 $\mu g/cm^2$ (Ripon), and 0.0401 $\mu g/cm^2$ (Porterville).

Methyl paraoxon residue levels were much lower than methyl parathion residue levels. Average methyl paraoxon residue levels after the fourth application were all below the LOQ (0.01 $\mu g/cm^2$). Residue levels remained below the LOQ (0.01 $\mu g/cm^2$) throughout the sampling period at Ripon, but were detected above the LOQ (0.01 or 0.001 $\mu g/cm^2$) at various sampling intervals at the other two field sites. The maximum average methyl paraoxon residues occurred on fifth day after the fourth application in Fresno (0.0265 $\mu g/cm^2$) and on the third day after the fourth application in Porterville (0.0175 $\mu g/cm^2$). Residue values on the last day of sampling (42 days after the fourth application in Fresno and 40 days after the fourth application in Porterville) were less than the LOQ (0.001 $\mu g/cm^2$) at Fresno, and 0.00112 $\mu g/cm^2$ at Porterville. The study author states that the intermittent detection of the methyl paraoxon residue levels precludes a meaningful analysis of the data.

SRD Sample Residues

The maximum average dislodgeable soil methyl parathion residues occurred immediately after the third application in Fresno (341 $\mu g/g$), the first application in Ripon (165 $\mu g/g$), and the fourth application in Porterville (91.8 $\mu g/g$). Residues were corrected for moisture content. Average methyl parathion residue values after the fourth application were 65.8 $\mu g/g$ (Fresno), 21.6 $\mu g/g$ (Ripon), and 91.8 $\mu g/g$ (Fresno). The average residue values varied significantly from site to site following each application. Residue values did not decline below the LOQ at any of the sites. Residue values on the last day of sampling (35 days after the fourth application) were 0.95 $\mu g/g$ (Fresno), 1.03 $\mu g/g$ (Ripon), and 0.241 $\mu g/g$ (Porterville).

Methyl paraoxon residue levels were much lower than methyl parathion residue levels. Average methyl paraoxon residue levels after the fourth application were all below the LOQ (0.5 $\mu g/g$). Residue levels remained below the LOQ (0.5 or 0.05 $\mu g/g$) throughout the sampling period at Fresno and Ripon, but were detected 8 hours after the fourth applicaton in Porterville (0.875 $\mu g/g$) before they declined below the LOQ. The maximum average methyl paraoxon residues occurred immediately prior to the third application in Fresno (3.09 $\mu g/g$), immediately after the second application in Ripon (2.73 $\mu g/g$), and 8 hours after the fourth applicaton in Porterville (0.875 $\mu g/g$). As with the DFR samples, the study author states that the intermittent detection of the methyl paraoxon residue levels precludes a meaningful analysis of the data.

Sample Calculations

Statistical procedures performed on the residue data included calculation of arithmetic mean, the range, and corresponding standard deviation. Linear regression analysis was applied to GC calibration curves to determine the slope, y-intercept, and correlation coefficient values. Actual DFR residues were transformed to $\mu g/cm^2$ by dividing the actual residues by 400 cm^2/sample. Corrected SRD residues were transformed to residues per $\mu g/cm^3$ by multiplying the total μg/gram found by the total grams collected and then dividing the total corrected μg found by the total cm^3 of soil collected. Residues were not corrected for moisture content. Results from the field fortifications were corrected by the mean recovery from concurrently analyzed freshly fortified control samples. Field sample residues were corrected by the overall mean corrected field fortification recoveries for the respective analytes and sites if recoveries were less than 100 percent. Only residues greater than the LOQ were corrected.

Linear regression analyses were performed by the study author on the average methyl parathion DFR ($\mu g/cm^2$) and SRD data ($\mu g/cm^3$). (Analyses were not performed for methyl paraoxon residues due to their intermittent detection which precluded meaningful analysis and calculation of half-life.) First order kinetics were used to predict the residue half-lives (Table 4). A separate dissipation model was generated for each field site beginning with samples collected immediately after the fourth application through 42 days (Fresno), 21 days (Ripon), and 40 days (Porterville) after the fourth application for DFR samples. Samples collected immediately after the fourth application through 35 days after the fourth application at all three field sites were included for SRD samples. Microsoft's® Excel 2000 linear regression function was applied to the log (ln) transformed data. Regression analyses predicted dissipation half-lives for methyl parathion of 7.76 days (Fresno), 5.41 days (Ripon), and 6.28 days (Porterville) for DFR. Dissipation half-lives of 13.50 days (Fresno), 8.76 days (Ripon), and 8.14 days (Porterville) were predicted for SRD.

Versar also used average DFR and SRD values in conducting linear regressions for the three field sites. The regressions were performed using the total residue level in each sample (sum of methyl parathion and methyl paraoxon), since methyl parathion and methyl paraoxon are assumed to have the same toxicity. DFR and SRD values beginning with the samples collected immediately after the fourth application through the last day of sampling were included. Data reported as total μg of analyte per gram of soil (corrected for moisture content) were used in the SRD regressions. The dissipation half-lives, as estimated by Versar, are shown in Table 4. Versar's values are similar to the values presented in the Study Report for the DFR samples and the SRD samples from Ripon. However, the SRD half-lives estimated for the Fresno and Porterville site are significantly different.

Table 4. Half-lives as Estimated by Excel Research Services and Versar, Inc.

Data Used for Regression	Matrix	Fresno Site		Ripon Site		Porterville Site	
		Half-life (days)	R^2	Half-life (days)	R^2	Half-life (days)	R^2
Excel Research Services	DFR[1]	7.76	0.80	5.41	0.80	6.28	0.83
Methyl Parathion	SRD[2]	13.50	0.57	8.76	0.81	8.14	0.68
Versar, Inc.	DFR[1]	7.78	0.80	5.41	0.80	6.46	0.84
Total Residues	SRD[3]	5.33	0.86	8.27	0.80	4.31	0.85

Footnotes:

1 $\mu g/cm^2$, ln

2 $\mu g/cm^3$ (not corrected for soil moisture), ln

3 $\mu g/g$ (dry weight), ln

NOTE: Includes average residue data through the last day of sampling at all three field sites.
Total Residues = Methyl parathion and methyl paraoxon.

Compliance Checklist

Compliance with OPPTS Series 875, Occupational and Residential Exposure Test Guidelines, Group B: Postapplication Exposure Monitoring Test Guidelines, 875.2100, Foliar Dislodgeable Residue Dissipation: Agricultural, and 875.220, Soil Residue Dissipation, and Part C - QA/QC, is critical. The itemized checklist below describes compliance with the major technical aspects of OPPTS 875.2100 and Part C - QA/QC, and is based on the "Checklist for Residue Dissipation Data".

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

- *Dislodgeable foliar residue (DFR) data and soil residue dissipation (SRD) data should be collected from at least three geographically distinct locations for each formulation.* This criterion was met. DFR and SRD data were collected at three locations in California. In 1997, California produced 269 tons of walnuts, 100 percent of the total U.S. production.

- *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 also analyzed.

- *Site(s) treated should be representative of reasonable worst-case climatic conditions expected in the intended use areas.* This criterion was met. When compared to the historical meteorological data, air temperatures were normal at all three test sites. However, rainfall was above normal in October, and below normal for November and December at all test sites.

- *End use product applied by application method recommended for the crop. Application rate given and should be at the least dilution and highest, label permitted, application rate.* These criteria were met. A Special Local Needs product label was provided in the Study Report. Four applications were made using the maximum label rate of 8 pints of formulated product per acre or 2.0 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. The times chosen for the study represented a summer/fall growing season in California. Applications were made during August-October in Fresno and Porterville, and during September-November in Ripon.

- *If multiple applications are made, the minimum allowable interval between applications should be used.* This criterion was met. The product label states that the minimum spray interval is 21 days. Four applications were made at 21-day intervals with one exception. At the Ripon test site, the interval between the second and third applications was 29 days due to wet soil conditions from rainfall and excessive winds.

- *Sampling should be sufficient to cover three half-lives and establish a dissipation curve.* This criterion was met. The half-lives calculated for the DFR residue levels by the study author (methyl parathion) and Versar (total residue) were very similar, 7.76 and 7.78 days (Fresno), 5.41 and 5.41 days (Ripon), and 6.28 and 6.46 days (Porterville), respectively. Half-lives calculated for the SRD residue levels by the study author (based on $\mu g/cm^3$) and Versar (based on $\mu g/g$ found) varied significantly at two of the test sites, 13.50 and 5.33 days (Fresno), 8.76 and 8.27 days (Ripon), and 8.14 and 4.31 days (Porterville), respectively. DFR samples were taken for 42 days (Fresno site), 21 days foliage, 35 days soil (Ripon site) and 40 days (Porterville site) after the last application. DFR and SRD residue values of methyl parathion did not decline below the LOQ at any of the test sites.

- *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 readings, wind speed and direction, cloud cover, and soil temperature and moisture were presented in the report for the days of application at each test site. Daily/monthly air temperature readings, and precipitation data were provided for the duration of the study. Average 10-year or 30-year historical meteorological data (monthly air temperature and precipitation) were also provided. The statement of GLP Compliance prepared for the study states that weather data (current and/or historical) were not collected or documented per the GLP regulations.

- *Reported residue dissipation data in conjunction with toxicity data should be sufficient to support the determination of a reentry interval.* This criterion was not met. No toxicity data were provided in this Study Report. Only residue dissipation data were presented.

- *Residue storage stability, method efficiency (residue recovery), and limit of quantitation (LOQ) should be provided.* These criteria were met. Laboratory and field fortification recovery values are provided in the Study Report. Storage stability data from a previously conducted study indicated that methyl parathion and methyl paraoxon were stable in DFR samples. Storage stability in SRD samples was demonstrated using the fortified field samples. The analytical method used for the analysis of DFR samples had a LOQ of 0.01 $\mu g/cm^2$ for both methyl parathion and methyl paraoxon. Select DFR samples were analyzed with a modified method with an LOQ of 0.001 $\mu g/cm^2$. The analytical method used for the analysis of SRD samples had a target LOQ of 0.05 ppm ($\mu g/g$) for each analyte. When methyl parathion residues exceeded 10 ppm, the LOQ for methyl paraoxon was adjusted to 0.5 ppm due to method limitations.

- *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. Soil samples were collected from six subplots and composited into one sample per replicate. Triplicate soil samples were collected from the treated plot and a single soil sample was collected from the untreated control plot.

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

- *The soil sampling technique should be appropriate to the exposure scenario of concern (e.g., surface soil sampling for most human activities involving contact with surface soils, and soil core sampling for activities such as potato harvesting and nursery stock transplating where exposure to subsurface soils can occur.* This criterion was met. Soil samples were collected using a hand-held vacuum or scooping method, depending on the conditions of the soil surface.

- *Soil texture and water content should be characterized. Soil samples should be sieved prior to analysis.* These criteria were met. Soil cores (0-12 inch depth) were collected at each field site. Soil types found at each site were Sandy Loam (Fresno and Ripon), and Loam (Porterville). The percent moisture at 1/3 bar/15 bar was 10.2/3.4 (Fresno), 11.5/NA (Ripon), and 22.1/8.7 (Porterville). Additional characterization information included: (1) percent sand, silt, clay; (2) percent organic matter; (3) pH; (4) cation-exchange capacity; and (5) bulk density. The percentage of water in each sample was determined based on drying and weighing an aliquot of wet soil to determine water loss. A 100-mesh screen was used to select the required, filtered dust particles 147 microns in size or smaller.

Other issues noted are the following:

- The west side of the first three trees in the outer row were sprayed twice at the second application at the Ripon test site due to tractor operator error. The study author anticipated minimal impact since the spray was directed towards the outside of the plot.

- The high areas of the trees were not sampled for DFR samples. The study author anticipated no adverse effect.

- Leaf discs and soil samples were not placed in ice chests containing wet or substitute ice during interim storage from the field to the field laboratory during the Postapplication 4 and 8 hours after the fourth application sampling events at Ripon. In addition, the leaves were wet from dew and/or rain. The study author anticipated no adverse effect.

- The final weights of the SRD samples were not recorded at the 7-day through 35-day, postapplication sampling events at the Porterville test site. An approximate total weight was recorded based on the weight of one sample jar. The study author anticipated no adverse effect.

- The Statement of GLP Compliance prepared for the study states that weather data were not collected per the GLP regulations.