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

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

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

August 1, 2001
MEMORANDUM

SUBJECT: Secondary Review of "Foliar Dislodgeable Residue Study: Determination of Dislodgeable Foliar Residues in Sugarcane and Tobacco Treated with *PROWL®* 3.3 EC Herbicide." MRID 449699-02. PC Code 108501. DP Barcode D262264.

FROM: Christina Jarvis, Environmental Protection Specialist Christina Jarvis 8/1/01
Reregistration Branch 2
Health Effects Division (7509C)

THROUGH: Alan Nielsen, Branch Senior Scientist A. Nielsen 8/1/01
Reregistration Branch 2
Health Effects Division (7509C)

TO: Mark Perry, Chemical Review Manager
Product Reregistration Branch
Special Review and Reregistration Division (7508W)

Attached is a review of the dislodgeable foliar residue study on sugarcane and tobacco submitted by American Cyanamid Company as confirmatory data. This review was completed by Versar, Inc. on December 22, 2000, under supervision of the Health Effects Division (HED). It has undergone secondary review in HED and has been revised to reflect current Agency policy.

(1)

Introduction

This report reviews a Dislodgeable Foliar Residue (DFR) study on sugarcane and tobacco submitted by American Cyanamid Company in support of reregistration requirements for pendimethalin. The requirements for this DFR study are specified by the EPA's OPPTS Series 875, Occupational and Residential Exposure Test Guidelines, Group B: Postapplication Exposure Monitoring Test Guidelines, Dislodgeable Foliar Residue Dissipation: Agricultural (Guideline 875.2100).

Summary

DFR data were collected in one geographical location per crop (i.e., sugarcane grown in Louisiana and tobacco grown in North Carolina). A layby application (ground-directed spray) of an aqueous solution of PROWL 3.3EC herbicide was made to established (10-leaf, vegetative stage) sugarcane plants at the Louisiana site using a CO_2 backpack-mounted sprayer, at the maximum label application rate of 3.95 lb ai/A in a spray volume of 10.3 gal/A. A layby application was made to tobacco (10-12 leaf stage) at the North Carolina site using a tractor-mounted cone tank sprayer, at the maximum label application rate of 1.0 lb ai/A in a spray volume of 10.16 gal/A. Residues samples were collected by leaf punch from high, medium, and low areas of the plants at the following intervals: one day before application, immediately after application, 12 hours after application, and one, three, seven, and 14 days after treatment (DAT).

Residues of pendimethalin dislodged from the sugarcane leaf samples were all less than the LOQ of 10.0 ng/cm^2. However, the Agency notes that the use of a CO_2 backpack-mounted sprayer may not be representative of typical layby application methods to sugarcane, as it is unlikely that a pesticide applicator would use hand-held equipment to treat sugarcane, a high acreage crop. It is uncertain what effect this application method may have had on residue values.

Residues of pendimethalin dislodged from all but one of the tobacco leaf samples were less than the LOQ of 10.0 ng/cm^2. One of the triplicate samples at 0.5 DAT returned 92 ng/cm^2 pendimethalin.

Conclusion

In summary, the pendimethalin dislodgeable foliar residue study completed in support of regulatory requirements contained the following omissions and flaws with respect to the 875.2100 guidelines:

- *Dislodgeable foliar residue (DFR) data to be collected from at least three geographically distinct locations for each formulation.* This criterion was <u>not</u> met. The sugarcane study was conducted at one geographic location in Louisiana, and the tobacco location was conducted at one geographic location in North Carolina.

- *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 not met. The authors did not discuss or consider breakdown products.

- *If multiple applications are made, the minimum allowable interval between applications should be used.* This criterion was partially met. PROWL® 3.3 EC was only applied once at each of the test sites. The label permits a second application per growing season for sugarcane, but only one application is specified for tobacco per growing season.

In addition, the study states that tank mix samples were taken at the North Carolina site prior to the application to confirm the concentration and uniformity of the spray solution. The study also states that tank mix samples were taken prior to the *third* application; however, there was only one application identified in the report. The Agency requests clarification of this issue from the registrant.

Pending clarification of the above-mentioned issue, HED concludes that the pendimethalin dislodgeable foliar residue study conducted by American Cyanamid Company in support of reregistration requirements is an acceptable study.

MEMORANDUM

TO: Christina Jarvis **cc:** 110082.1000.00101

FROM: Jim Buchert, Diane Forrest

DATE: December 22, 2000

SUBJECT: Review of *Foliar Dislodgeable Residue Study: Determination of Dislodgeable Foliar Residues in Sugarcane and Tobacco Treated with PROWL® 3.3 EC Herbicide* - MRID #449699-02

This report reviews *Foliar Dislodgeable Residue Study: Determination of Dislodgeable Foliar Residues in Sugarcane and Tobacco Treated with PROWL® 3.3 EC Herbicide* submitted by American Cyanamid Company in support of reregistration requirements for *Pendimethalin*. The requirements for this study are specified by 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, Dislodgeable Foliar Residue Dissipation: Agricultural. The following information may be used to identify the study:

Title:	*Determination of Dislodgeable Foliar Residues in Sugarcane and Tobacco Treated with PROWL® 3.3 EC Herbicide*, 154 pages	
Sponsor:	Frederick L. Groya, Ph.D. American Cyanamid Company Agricultural Products Research Division P.O. Box 400 Princeton, NJ 08543-0400	
Performing Laboratories: (Field Study)	Nelson Prochaska R&D Research Farm, Inc. 7033 Highway 103 Washington, LA 70589	Mike Striebel American Agricultural Services, Inc. 7174 Gourd Branch Road Lucama, NC 27851
Analytical Laboratory:	Toreen Bixler Maxim Technologies 140 Telegraph Road Middleport, NY 14105	
Study Director & Author:	Arthur Kleiner American Cyanamid Company	
Study Completion Date:	July 7, 1999	
Identifying Codes:	Study Numbers: RES 98-065 and RES 98-066; MRID #449699-02	

Executive Summary

This report reviews a study submitted by American Cyanamid Company characterizing the dissipation of pendimethalin residues from sugarcane and tobacco leaves in Louisiana and North Carolina after one layby application of PROWL® 3.3 EC. This herbicide is formulated as an emulsifiable concentrate with a nominal active ingredient (ai) content of 37.4 percent. The study quantifies pendimethalin as dislodgeable foliar residues.

At each test site, three plots were treated with one layby application of PROWL® 3.3 EC at the maximum label rate of 4.0 lb. ai/A for sugarcane and 1.0 lb ai/A for tobacco. The spray volume used during each application was approximately 10 gal/A. Pendimethalin residues were below the LOQ (i.e., 10 ng/cm^2) for all samples except one. Therefore, Versar did not further analyze the data.

The study report had some deviations from the Environmental Protection Agency's (US-EPA) OPPTS Series 875, Occupational and Residential Exposure Test Guidelines, Group B: Postapplication Exposure Monitoring Test Guidelines, 875.2100, Dislodgeable Foliar Residue Dissipation: Agricultural. The most important deviations from EPA-OPPTS and good practice guidelines were:

1. DFR data were collected from only one, instead of the usual three, geographically distinct locations for each crop.

2. Tank mix sample analytical results (raw data) could not be located for verification of percent recovered.

3. No information was provided on the type of soils found at the test sites. Maximum application rates specified in the PROWL® 3.3 EC Herbicide label depend on soil type.

STUDY REVIEW

Study Background

This report reviews a dislodgeable foliar residue (DFR) study submitted by American Cyanamid Company in support of reregistration requirements for pendimethalin (EPA Reg. No. 241-337). PROWL® 3.3 EC Herbicide contains 3.3 lbs. ai/gal and is formulated as an emulsifiable concentrate with a nominal active ingredient content of 37.4 percent. The product controls most annual grasses and some broadleaf weeds by preventing weed germination. It does not control established weeds. The chemical name of pendimethalin is (N-(1-Ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine) and the CAS number is 40487-42-1. The chemical structure of this compound was not provided in the Study Report, but is readily available in reference texts.

The study presents DFR data collected in one geographical location per crop (i.e., sugarcane grown in Louisiana and tobacco grown in North Carolina). The field phase for the Louisiana test site was conducted under the supervision of R&D Research Farm, Inc., Washington, Louisiana The field phase for the North Carolina test site was conducted under the supervision of American Agricultural Services, Inc., Lucama, North Carolina. Sample analyses for both sites were performed by Maxim Technologies, Middleport, New York. Samples were collected at both sites between July 6, and July 21, 1998. All sample analyses were conducted between December 4, and December 18, 1998.

Test Plot

One test site was set up in Washington, (Washington Parish) Louisiana at the facilities of R&D Research Farm, Inc. The second test site was set up in Lucama, (Wilson County) North Carolina at the facilities of American Agricultural Services, Inc. A layby application (ground directed spray) of an aqueous solution of PROWL 3.3EC herbicide was made to established (10-leaf, vegetative stage) sugarcane plants at the Louisiana site, and to tobacco (Flu Cured, 10-12 leaf stage) at the North Carolina site. Sampling took place at both sites between July 6, and July 21, 1998. Herbicide application, irrigation, and rainfall information for both sites is provided in Table 1. No information was provided on the type of soils found at the test sites. Maximum application rates specified in the PROWL® 3.3 EC Herbicide label depend on soil type.

<u>Washington, (Washington Parish) Louisiana site:</u>

Control and test plots were established at each test site. The treated plot at the Louisiana site was 72 feet long by 50 feet wide. The untreated control plot was 100 feet long by 36 feet wide. Both plots had been planted with established sugarcane (variety 845) in rows spaced 72 inches apart with 10 to 12 inch plant spacing within each row. For sampling, the treated plot was

divided into three equal areas of four 50-foot long rows. One replicate sample was taken from within each of the three subplot areas. Approximately 100 feet between the untreated (control) plot and the treated plot was established at the testing location. [A sample plot diagram is provided on page 57 of the study report.] Prior to the test (on May 14, 1998), ASULOX (ai = asulam or methyl sulfanilylcarbamate) herbicide (3.34 lbs ai/gal) had been applied to the test plots at a rate of 8 pints/Acre.

Lucama, (Wilson County) North Carolina site:

The treated plot at the North Carolina site contained 2 areas 150 feet long by 12 feet wide, parallel to each other and separated by 26 feet, 10 inches. The untreated control plot was 75 feet long by 12 feet wide. The nearest treated plot area was separated from the untreated (control) plot by 302 feet. Both plots had been planted with *Flu Cured* variety tobacco in 36 inch rows with 18 inch plant spacing within each row. For sampling, the treated plot was divided into three equal areas as follows: each 150 by 12 foot plot was divided into a 100 by 12 foot and a 50 by 12 foot section; the 100 by 12 foot section of one plot was designated as Subplot A; the 100 by 12 foot section of the other plot was designated as Subplot B; and the two 50 by 12 foot sections together were designated as Subplot C. A sample plot diagram is provided on page 125 of the study report. Prior to this test (on April 30, 1998), DEVRINOL® 50 DF (ai = napropamide or N,N-diethyl-2-(1-naphthyloxy)propanamide) herbicide was applied to the test site.

Table 1. Cultural Practices and Rainfall Conditions

Test Site	Herbicide Use During Sampling Year	Irrigation/Rainfall During Sampling Period
Louisiana	ASULOX herbicide applied to the test plots on May 14, 1998 (ai = asulam or methyl sulfanilylcarbamate)	0.37 inches rain DAT-7: 0.29 inches rainfall DAT-9: 0.07 inches rainfall no irrigation
North Carolina	DEVRINOL® 50 DF herbicide was applied to the test site on April 30, 1998 (ai = napropamide or N,N-diethyl-2-(1-naphthyloxy)propanamide)	2.12 inches rain DAT-1: 0.48 inches rainfall DAT-3: 1.52 inches rainfall no irrigation

Note: Sampling took place at both sites between July 6, and July 21, 1998.

Meteorology

Weather data were collected by on-site Campbell Scientific weather stations located approximately 200 yards from their respective test sites. No irrigation was applied to the test plots from the time of application to the last sampling. The study report provides daily rainfall data and average daily wind speed for July, 1998, the month of application and sampling. The study report also provides daily minimum and maximum data for: air temperature; soil temperature; and relative humidity, for July, 1998. The Louisiana weather station also collected

average daily wind direction data. Sampling took place at both sites on July 6, 7, 8, 10, 14, and 21, 1998. Rainfall occurred at the Louisiana test site on the day before treatment, and on DAT (day after treatment) 7 and 9. Rainfall occurred at the North Carolina test site on DAT-1 and DAT-3. (See Table 1.)

Materials and Applications

A product label was not provided in the study report. Versar obtained a copy of the EPA Reg. No. 241-337 label for PROWL® 3.3 EC herbicide in order to verify the maximum label specified application rate and other application instructions. PROWL® EC 3.3 is an emulsifiable concentrate containing 3.3 pounds active ingredient per gallon. The label specifies an application spray volume of at least 10 gallons per acre.

Washington, Louisiana (sugarcane) site:

One layby (ground directed spray) application of PROWL® 3.3 EC herbicide was applied to established sugarcane (10-leaf vegetative stage) at a rate of 3.95 lb ai/A in a spray volume of 10.30 gal/A. This is the maximum label application rate for sugarcane in Hawaii. The maximum label application rate for sugarcane not in Hawaii is 2.97 lb ai/A. Therefore, the application rate used in this study (Hawaii rate of 3.95 lb ai/A) exceeded the maximum rate for a single application at the Louisiana site (2.97 lb ai/A). Irrigation was not applied. The label specified a maximum of 5.94 lb ai/A in one growing season, or up to 2 applications per growing season, in heavy clay soils. However, only one application was made in this study, and no information on test site soil characteristics was provided.

PROWL® 3.3 EC was applied to the soil between the rows of established sugarcane in the treated plot. The test substance was broadcast about 18 inches above the base of the plants using a 1-nozzle boom attached to a CO_2 backpack-mounted sprayer. The nozzle was a size D2 Delevan brand flood type, the swath width was 6 inches, and the operating pressure was 34 psi. The equipment was calibrated before application, and one pass was made over each of the eleven rows between the sugarcane plants.

The label specifies that for sugarcane, PROWL® 3.3 EC must be thoroughly and uniformly incorporated into the soil with either mechanical incorporation or with rainfall or irrigation within 7 days of application. The study report does not mention any mechanical incorporation, however, the report specifies that no irrigation took place during the time of the study. Rainfall occurred at the test site 1 day before application, and on DAT-7.

Lucama, North Carolina (tobacco) site:

For North Carolina, the label specifies layby application rates for tobacco ranging from 0.50 to 1.0 lb ai/A depending on the soil texture. The label specifically states that the "the spray should not be allowed to contact tobacco plants." One layby (ground directed spray) application

of PROWL® 3.3 EC herbicide was applied to tobacco (10-12 leaf stage) at the maximum rate of 1.0 lb ai/A in a spray volume of 10.16 gal/A. Irrigation was not applied, however, a total of 2.12 inches of rain fell between DAT-0 and DAT-3. The label does not appear to permit more than one application per growing season. No information on test site soil characteristics was provided.

One layby directed application of PROWL® 3.3 EC was applied to the soil between the rows of tobacco in the treated plot areas. The test substance was broadcast about 16 inches above the base of the plants (soil surface) using a 3-nozzle boom attached to a tractor-mounted cone tank sprayer. The flat fan nozzles were size 9501E, and the source of pressure (25 psi) was a centrifugal pump. The nozzles were spaced 36 inches from each other to create a swath width (band) of 18 inches between the four rows in the two treated plot areas. The equipment was calibrated before application, and one pass was made over each of the two treated plot areas.

Sampling of Leaf Dislodgeable Residue Samples

Samples were collected at the following intervals: 1 day before application, immediately after application; 12 hours after application; and DAT-1, 3, 7, and 14. Leaf material was sampled using a 2.54 cm diameter leaf punch. At each sampling, 40 discs, each with a total surface area of 10 cm^2 were taken to provide a sample with a total surface area of 400 cm^2. Samples were obtained by taking four discs from each of 10 plants. A similar number discs were reportedly taken from high, medium, and low areas of the plants. One replicate sample was taken from each of the 3 treated subplots and from the untreated control plot at each sampling interval using a zig-zag pattern. In the treated plot, samples were taken from only the two inner rows within each subplot. The pretreatment samples, at the Louisiana site, were collected randomly from the plot to be treated in one diagonal pass traversing the entire plot area. The manner in which the pretreatment samples were collected at the North Carolina site was not discussed. At the Louisiana site, separate leaf punches were used to obtain samples from the control and treated plots, and the control plot was always sampled first. At the North Carolina site, a single leaf punch, cleaned with soap and water and acetone between samplings, was used. On the day before treatment, one control and six pretreatment samples for field fortification were taken.

Immediately after collection, samples were placed in coolers with blue ice until they were dislodged. The leaf samples were dislodged with 0.01% Aerosol® OT, and the resulting solutions were placed in freezers within 2 hours of sampling. Dislodging solutions were prepared fresh on each day they were needed. Leaf samples were dislodged in the jars in which they were collected. One hundred mL of the 0.01% Aerosol® OT solution was added to each jar containing the leaf material. At the Louisiana site, the jars were capped and placed on a Gilson shaker table operating at 180 cycles per minute for about 10 minutes. (Note: The Field Phase Report [page 50] states that 180 cycles per minute was used, however, a protocol deviation [page 41] states that 135 cycles per minute will be used because that is the maximum for the shaker.) At the North Carolina site, the jars were capped and placed on a Eberbach 5850 reciprocating

shaker operating at 200 cycles per minute for about 10 minutes. The leaf material was separated from the solution by decanting the solution into a clean plastic coated glass jar. At the Louisiana site, 500 mL jars were used, and at the North Carolina site, 1000 mL jars were used. Any fallen leaf material was returned to the original sample jar for the second dislodging. Another 100 mL of the 0.01% Aerosol® OT solution was added to the leaf material and the dislodging process repeated. The first and second dislodging solutions were combined. Teflon-lined caps were loosely screwed onto the sample jars which were placed at an angle in the freezer. The caps were tightened and sealed with tape after the samples were frozen.

QA/QC

Sample Handling & Storage

Leaf samples were dislodged with 0.01% Aerosol® OT. The resulting solutions were placed in freezers within 1.5 to 2 hours of sampling, and they were maintained there until shipment. Daily freezer temperatures were monitored with a HOBO system at the Louisiana site and by the use of analog temperature probes at the North Carolina site. The temperature of the freezers remained below freezing for the duration of the time that samples were kept there. The samples were stored for a maximum of 13 and 15 days, respectively, at the Louisiana and North Carolina sites.

On July 10 and 23, 1998, the samples (in plastic-coated bottles) from the Louisiana site were placed in boxes and transported to American Cyanamid Company (ACCO) in Princeton, NJ by ACDS freezer trucking service. Frozen product and tank-mix samples were packed separately and included in the July 10, 1998 shipment. The samples (including frozen product and tank-mix samples) from the North Carolina site were shipped to ACCO on July 21, 1998. All samples were placed in freezers upon receipt, and on November 18, 1998, all of the frozen Aerosol® OT samples were shipped via Federal Express overnight delivery to Maxim Technologies in Middleport, New York.

Sample History

Table 4 of the Field Phase Report (page 55) and Table I of the Analytical Phase Report (page 71) provide information regarding sample handling and analysis of the Louisiana site samples. The maximum time from sample collection to analysis was 165 days. Table 4 of the Field Phase Report (page 131) and Table I of the Analytical Phase Report (page 147) provide information regarding sample handling and analysis of the North Carolina site samples. The maximum time from sample collection to analysis was 163 days. The study protocol mentions that a chain-of-custody will be used, however, a formal chain-of-custody was not mentioned for either site in their respective portions of the study report.

Tank Mix Analyses

Tank mix samples were taken at the Louisiana site prior to application to confirm the concentration and uniformity of the spray solution. The study report states (on pages 15 and 48) that recovery averaged 111 percent. A single tank mix sample is identified on the sampling schedule on page 59, however, the analytical results of this sample could not be found in the table of results. Tank mix samples were taken at the North Carolina site prior to the application to confirm the concentration and uniformity of the spray solution. [Note: The Study Report states [on page 89] that tank mix samples were taken prior to the *third* application, however, there was only one application identified in the report. The Agency requests clarification of this issue]. The study report states (on pages 89 and 124) that recovery averaged 116 percent. A single tank mix sample is identified on the sampling schedule on page 135, however, the analytical results of this sample could not be found in the table of results.

Analytical Methodology

The analytical methodology used for PROWL® 3.3 EC leaf residue analysis of the Louisiana site samples was specified in the study report as: American Cyanamid Draft Method M 3239 (dated 09/18/98) entitled, *"CL 92553 (pendimethalin): Gas Chromatography (GC) Method M 3239 for the Determination of CL 92553 Dislodgeable Residues from Sugarcane Leaves."* The study report does not describe many aspects of the analytical methodology, including sample extraction, clean-up, and validated range. [Note: Versar reviewed MRID #449699-03 which presented very marginal method validation data and described sample extraction and clean-up steps. For method validation, the field samples were thawed, and transferred to glass beakers. Next, the samples were fortified with known amounts of pendimethalin, dissolved in acetone. The pendimethalin used was analytical grade, of known purity (~98.4% pure), obtained from American Cyanamid. The reference standard was stored under refrigeration at 3°C ± 4C°.] The methodology used on the North Carolina site samples is essentially identical, but is referred to as M 3238, and is applicable to tobacco leaves.

Leaf material (400 cm^2 total surface area) was sampled using a 2.54 cm diameter leaf punch. Samples were obtained by taking four discs from each of 10 plants. One replicate sample was taken from each of the 3 treated subplots and from the untreated control plot at each sampling interval. On the day before treatment, one control and six pretreatment samples for field fortification were taken.

Control sugarcane leaf wash samples were prepared at Maxim Technologies on August 27 and 28, 1998. Control tobacco leaf wash samples were prepared at Maxim Technologies on August 19, 1998. The samples were stored frozen at -15°C until analysis. According to the study report, the methods were validated at Maxim Technologies. The average recovery was 101 percent from the sugarcane leaf validation study, and 106 percent from the tobacco leaf validation study for fortification levels of 10 and 100 ng/cm^2.

Leaf samples were dislodged in the jars in which they were collected. One hundred mL of the 0.01% Aerosol® OT solution was added to each jar containing the leaf material. The jars

were capped and placed on a shaker table for about 10 minutes. The leaf material was separated from the solution by decanting the solution into a clean plastic-coated glass jar. Any fallen leaf material was returned to the original sample jar for the second dislodging. Another 100 mL of the 0.01% Aerosol® OT solution was added to the leaf material and the dislodging process repeated. The first and second dislodging solutions were combined. Teflon-lined caps were loosely screwed onto the sample jars which were placed at an angle in the freezer. The caps were tightened and sealed with tape after the samples were frozen.

From Versar's review of MRID #449699-03, it appears that next, 5 mLs saturated NaCl were added, and the solution was extracted twice into 50 mLs methylene chloride, using a separatory funnel. The organic layers were collected, combined, subjected to roto-evaporation, then 5 mLs methanol was added (if residual water was found to exist), and the extract evaporated to dryness. Finally, 8 mLs acetone was added, the sample was sonicated, filtered through 0.22 µM nylon filters, and an aliquot injected into a gas chromatograph equipped with a nitrogen phosphorous detector. The rest of the sample was frozen at less than -15°C.

The GC system used at Maxim Technologies, Inc. was equivalent to that listed in Methods M 3238 and M 3239. Gas Chromatography conditions were most likely identical for both tobacco and sugarcane methods. The only uncertainty was that the sample run time and the inlet temperature were not specified for tobacco. The run time for sugarcane was 19.2 minutes. Both the Tobacco and the Sugarcane Aerosol® OT leaf wash extracts were injected on a Hewlett Packard 5890 Gas Chromatograph equipped with a nitrogen-phosphorous detector. The injection volume was 1 µL and the retention time for pendimethalin was 9.2 minutes for both sugarcane and tobacco samples. Gas chromatographic data were processed using CLAS.

Representative chromatograms of analyte standards were provided in the study report. representative chromatograms provided for review showed good peak separation and reasonably sharp peaks.

Limits of Detection (LOD) & Limit of Quantitation (LOQ)

The Limit of Quantitation (LOQ) was reported to be 10 ng/cm^2. The limit of detection was reported as 0.8 ng/cm^2 for both the Louisiana sugarcane leaf samples, and for the North Carolina tobacco leaf samples.

Control Samples

Approximately 100 feet between the untreated (control) plot and the treated plot was established at the Louisiana site. At the North Carolina site, the nearest treated plot area was separated from the untreated (control) plot by 302 feet. Control samples were collected on the same days and just prior to collection of treated samples.

Concurrent Laboratory Recovery

The study report identified two fortification levels (10 and 100 ng/cm^2), and reported an average recovery of 86 ± 5.5 percent for tobacco DFR and 98 ± 6.1 percent for sugarcane DFR. Six fortified tobacco and six fortified sugarcane samples were tested.

Table 2. Average Laboratory Recoveries

Sample	Fortification Level (ng/ cm^2)	n	Mean Recovery (%)	Standard Deviation (%)	Coefficient of Variation (CV) (%)
Tobacco	10	3	81	4.2	5.1
Tobacco	100	3	90	1.7	1.9
Sugarcane	10	4	99	7.7	7.8
Sugarcane	100	2	98	2.1	2.2

Field Fortification Recovery

Two sets of triplicate leaf samples were fortified in the field on the day before application at 20 ng/cm^2 and 50 ng/cm^2. These fortified samples were prepared by adding 1 mL of an 8 µg/mL and a 20 µg/mL spiking solution, respectively, to pretreatment dislodging samples. The field fortified samples were stored and/or shipped, extracted and analyzed in the same manner as the frozen DFR samples.

The average field fortification recoveries were 102 ± 8.6 percent and 80 ± 7.2 percent, respectively for the Louisiana (Sugarcane) and North Carolina test (Tobacco) sites. Average recoveries for each fortification level for each study are summarized below in Table 3.

Table 3. Average Field Fortification Recoveries

Sample	Fortification Level (ng/cm^2)	n	Mean Recovery (%)	Standard Deviation (%)	Coefficient of Variation (CV) (%)
Tobacco	20	3	78	9.6	12.4
Tobacco	50	3	83	4.5	5.4
Sugarcane	20	3	109	4.3	3.9
Sugarcane	50	3	94	1.6	1.7

Storage Stability Recovery

The author of the study report cites American Cyanamid report LE 32202 to make the claim that PROWL® 3.3 EC has been demonstrated to be stable for 24 months at 25°C. The study report indicates that spiking solutions were prepared on June 23, 1998, then shipped to the test site on July 1, 1998. The spiking solutions were stored in a refrigerator until they were used to prepare the field fortified samples on July 6, 1998, one day prior to application. A freezer stability study was not initiated. Field fortified FDR samples remained in storage for a maximum of 165 days prior to analysis. Average recoveries at each field fortification level are provided in Table 3 above. Because the field data were almost entirely non-detect, field recovery data were not used for data correction.

Results

No linear regressions were performed for the data from either of the test sites. At the Louisiana site, residues of pendimethalin dislodged from sugarcane leaf samples were all less than the LOQ of 10.0 ng/cm^2. At the North Carolina site, residues of pendimethalin dislodged from all but one of the tobacco leaf samples were less than the LOQ of 10.0 ng/cm^2. One of the triplicate samples at 0.5 days after treatment returned 92 ng/cm^2 pendimethalin.

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. Additional data gaps identified in the study (not covered by the checklist) are also presented below:

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

- *Dislodgeable foliar residue (DFR) data to be collected from at least three geographically distinct locations for each formulation.* This criterion was not met. The sugarcane study was conducted at one geographic location in Louisiana. Louisiana ranked second in sugarcane production in 1997 and accounted for about 38 percent of the total US sugarcane production. The tobacco study was conducted at one geographic location in North Carolina. In 1997, North Carolina ranked first in tobacco production and accounted for about 43 percent of the total US tobacco crop.

- *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 not met. The authors did not discuss or consider breakdown products.

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No linear regressions were performed for the data from either of the test sites. At the Louisiana site, residues of pendimethalin dislodged from sugarcane leaf samples were all less than the LOQ of 10.0 ng/cm^2. At the North Carolina site, residues of pendimethalin dislodged from all but one of the tobacco leaf samples were less than the LOQ of 10.0 ng/cm^2. One of the triplicate samples at 0.5 days after treatment returned 92 ng/cm^2 pendimethalin.

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. Additional data gaps identified in the study (not covered by the checklist) are also presented below:

- *Typical end use products of the active ingredient used.* This criterion was met.
- *Dislodgeable foliar residue (DFR) data to be collected from at least three geographically distinct locations for each formulation.* This criterion was not met. The sugarcane study was conducted at one geographic location in Louisiana. Louisiana ranked second in sugarcane production in 1997 and accounted for about 38 percent of the total US sugarcane production. The tobacco study was conducted at one geographic location in North Carolina. In 1997, North Carolina ranked first in tobacco production and accounted for about 43 percent of the total US tobacco crop.
- *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 not met. The authors did not discuss or consider breakdown products.

- *The choice of end-use product to test should be made considering the following factors: (1) availability in several different formulations; (2) liquid formulations (e.g. emulsifiable concentrates) are preferred; (3) watering-in is to be avoided; (4) product to be applied in a minimal amount of water; (5) product to be applied after mowing and watering; (6) application of the product should not be made within 24 hours of an expected rain event.* These criteria were met. The product is available in several different formulations, but only the emulsifiable concentrate was tested. The label specifies an application spray volume of at least 10 gal/A. The test sites used 10.16 gal/A and 10.30 gal/A. The study report did not mention if any mowing or watering occurred prior to application. Rainfall occurred during the first day after treatment at the North Carolina site.

- *Site(s) treated representative of reasonable worst-case climatic conditions expected in intended use areas.* This criterion was met. The sites and time chosen for the study represented the summer season in the Southeast region.

- *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 product label was not provided in the study report. Versar obtained a copy of the EPA Reg. No. 241-337 label for PROWL® 3.3 EC herbicide in order to verify the maximum label specified application rate and other application instructions. The application methods used were acceptable. The label specifies an application spray volume of at least 10 gal/A. PROWL® 3.3 EC herbicide was applied to established sugarcane at a rate of 3.95 lb ai/A in a spray volume of 10.30 gal/A. This is the maximum label application rate for sugarcane in Hawaii. The maximum label application rate for sugarcane not in Hawaii is 2.97 lb ai/A. The label specifies an application rate for tobacco from 0.50 to 1.0 lb ai/A depending on the soil texture. PROWL® 3.3 EC herbicide was applied to tobacco (10-12 leaf stage) at the maximum rate of 1.0 lb ai/A in a spray volume of 10.16 gal/A. Irrigation was not applied at either site.

- *Applications occurred at time of season that the end-use product is normally applied to achieve intended weed control.* This criterion was met. The application was made after crops were transplanted to the field, as permitted by the label. PROWL® 3.3 EC can be applied preemergence through layby, and again in late summer or early fall for newly planted sugarcane. For tobacco, the label specifies application following last normal cultivation, usually 4 to 6 weeks after transplanting. The application in the study report occurred 7 weeks after transplanting tobacco.

- *If multiple applications are made, the minimum allowable interval between applications should be used.* This criterion was <u>partially</u> met. PROWL® 3.3 EC was only applied once at each of the test sites. The label permits a second application per growing season for sugarcane, but only one application is specified for tobacco per growing season.

- *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. Samples were collected at the following intervals: 1 day before application, immediately after application; 12 hours after application; and at DAT 1, 3, 7, and 14. Residues were all less than the LOQ of 10.0 ng/cm^2; therefore, in this case dissipation half-lives were not calculated.

- *Meteorological conditions including temperature, wind speed, daily rainfall, and humidity provided for the duration of the study.* This criterion was met. Daily rainfall data and average daily wind speed were collected for July, 1998, the month of application and sampling. Also, daily minimum and maximum data for: air temperature; soil temperature; and relative humidity were collected. The Louisiana weather station also collected average daily wind direction data.

- *Reported residue dissipation data in conjunction with toxicity data must be sufficient to support the determination of a reentry interval.* This criterion is not applicable. Half life values were not calculated since residues were all less than the LOQ of 10.0 ng/cm^2; therefore, REIs will default to the WPS. No toxicity data was provided with this study report.

- *Residue storage stability, method efficiency (residue recovery), and limit of quantitation (LOQ) provided.* These criteria were met. Laboratory recovery, and field fortification recovery values were provided in the report. The LOQ was 10.0 ng/cm^2 for pendimethalin. No separate storage stability test was conducted. Storage stability was demonstrated by acceptable field fortification recoveries.

- *Triplicate, randomly collected samples to be collected at each sampling interval.* This criterion was met. Three replicate samples (1 from each of the 3 treated subplots and 1 from the untreated control plot) were collected at each sampling interval at each site.

- *Control and baseline foliar or soil samples collected.* This criterion was met. No soil samples were collected for this study.

Pertinent data gaps and other issues critical to the scientific validity and regulatory acceptability (i.e., Series 875 Group B compliance) of the study, not already addressed, are presented below. The following issue was identified:

- After the leaf samples from the Louisiana site were dislodged twice with 100 mL of the 0.01% Aerosol® OT solution, the jars were capped and placed on a Gilson shaker table. The number of cycles per minute used is uncertain. The Field Phase Report states on page 50 that 180 cycles per minute was used, however, a protocol deviation on page 41 states that 135 cycles per minute will be used because that is the maximum for the shaker.