428759

Versar INC.

MEMORANDUM

TO: Al Nielsen EPA/OPP/OREB

cc: 2994.101 File
Tim Leighton
Jeff Evans

FROM: Jeff Dawson

DATE: September 11, 1995

SUBJECT: Transmittal of summary reviews of the chlorothalonil broccoli and cherry foliar dislodgeable residue studies (MRIDs 428759-03 & 02)

The chlorothalonil foliar dislodgeable studies on broccoli and cherries have been reviewed for adherence to Subdivision K guidelines. The review document and the studies are enlcosed in this package. Should you have any questions please call me at anytime.

Enclosures:

(1) *Determination of Dislodgeable Foliar Residues of Chlorothalonil and HCB From Bravo 720 Treated Broccoli Plants* (EPA MRID 428759-03/ISK Doc. # 5224-92-0069-CR-002)

(2) *Determination of Dislodgeable Foliar Residues of Chlorothalonil and HCB From Bravo 720 Treated Cherry Trees* (EPA MRID 428759-02/ISK Doc. # 5224-92-0069-CR-001)

(3) *Summary reviews of chlorothalonil broccoli and cherry foliar dislodgeable residue studies (MRIDs 428759-03 & 02)* Prepared and submitted by Versar, Inc. on September 11, 1995.

Versar INC.

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TO: Al Nielsen EPA/OPP/OREB

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SUBJECT: Summary reviews of the chlorothalonil broccoli and cherry foliar dislodgeable residue studies (MRIDs 428759-03 & 02)

Two studies were submitted in support of the registration requirements for the fungicide chlorothalonil formulated as Bravo 720, a liquid formulation containing 6.0 pounds per gallon of the active ingredient (54.0 % a.i. by weight). These requirements were specified by the U.S. Environmental Protection Agency, herein referred to as the Agency, under Subdivision K (i.e., Exposure: Reentry Protection) of the Pesticide Assessment Guidelines under 40 CFR 158 (i.e., U.S. EPA/1984, and U.S.EPA/1988).

The following information can be used to identify the two studies:

Titles:	(1) Determination of Dislodgeable Foliar Residues of Chlorothalonil and HCB From Bravo 720 Treated Broccoli Plants (2) Determination of Dislodgeable Foliar Residues of Chlorothalonil and HCB From Bravo 720 Treated Cherry Trees
Sponsor:	ISK Biotech Corporation 5966 Heisley Road P.O. Box 8000 Mentor, Ohio 44061-8000
Performing Laboratory:	Ricerca, Inc. Department of Environmental Sciences 7258 Auburn Road P.O. Box 1000 Painesville, Ohio 44077-1000
Author:	T.M. Formella
Report Dates:	(1) May 3, 1993 (2) May 14, 1993
Identifying Codes:	(1) EPA MRID 428759-03/ISK Doc. # 5224-92-0069-CR-002 (2) EPA MRID 428759-02/ISK Doc. # 5224-92-0069-CR-001

Each study is reviewed below on an individual basis. The broccoli study is reviewed first followed by a review of the cherry study.

BROCCOLI STUDY REVIEW

Chlorothalonil and HCB (hexachlorobenzene -- a manufacturing impurity) foliar dislodgeable residues were collected from treated broccoli plants after a series of Bravo 720 applications. The field portion of the study was conducted at the Ricerca, Inc. experimental farm located in Madison, Ohio and the analytical portion of the study was conducted at the Ricerca, Inc. laboratory facility in Painesville, Ohio. The field study was initiated on May 4, 1992 and was conducted through August 25, 1992. Treated and control plots were used in this study. Each plot consisted of 8 rows of plants each 100 feet long. Broccoli plants (i.e., *Green Comet* variety) were transplanted into these plots on May 15, 1992 at the 2 - 4 leaf growth stage. In this study, a total of eight Bravo 720 applications were made as a broadcast spray at approximately weekly intervals. The final application was made on July 8, 1992 after the harvestable broccoli heads had reached approximately 5 inches in diameter. Six of the eight applications were made at a rate of 1.5 pints/acre (i.e., 1.125 lb ai/acre) while the other two applications (i.e., #s 2 and 4) were made at a rate of 1.11 pints/acre (i.e., 0.8325 lb ai/acre). All applications were made by applying approximately 32 gallons per acre using a tractor drawn groundboom sprayer (i.e., John Deere Model 2640 and Demco Model RM Sprayer with Lurmark 03-F80 plastic nozzles at ~40 psi and 2.9 to 3.1 mph).

Foliar dislodgeable residue samples were collected on Day 0 (i.e., day of final application) and at 1, 2, 5, 8, 15, 22, 29, and 36 days after the final application. Five control and triplicate treated foliar dislodgeable residue (FDR) samples were collected from the control and treated plots at each sample interval. Three control replicates were analyzed as field control samples while the remaining two samples were reserved for concurrent laboratory analysis purposes. Each FDR sample contained 40 leaf disc punches collected using a Birkestrand 1.262cm diameter leaf punch (i.e., each sample represented a double-sided surface area of 100cm^2). Two rows were used to generate each sample while twenty punches were collected from a single row (i.e., 8 rows per plot were designated but perimeter rows serves as a buffer only and were not included in sample gathering). Leaf disc samples were collected in glass jars attached to the leaf punch device at various 90° positions around the center of the plants alternating down the rows of the sampled plots. After sampling, the jars were sealed with Teflon-lined lids and placed on "Blue ice" for shipment to the analytical laboratory where the samples were dislodged on the sample collection day and subsequently analyzed.

FDR samples were dislodged at the analytical laboratory by shaking in two sequential 100 mL aliquots of an aqueous surfactant solution prepared by adding 100 mL of water and 0.4 mL of a surfactant solution (i.e., 1:50 v:v dilution of Aerosol OT 75) to the glass jars containing the leaf disc samples and shaking them on a reciprocating shaker for approximately 10 minutes. This procedure was repeated and both 100 mL aliquots of surfactant solution were added to separatory funnels. After the dislodging procedures were complete, a 50 mL aliquot of pet ether was used to rinse the glass jars for quantitative transfer into the separatory funnels along with a 10 mL aliquot of an aqueous NaCl solution (20 % w:v). After the partition, the organic layer was collected, concentrated, and solvent exchanged then passed through a Florisil clean-up column. Chlorothalonil and HCB residues were then quantified using a gas chromatograph equipped with an electron capture detector and a DB-5 capillary column. The LOQ for chlorothalonil and HCB respectively, based on recovery at the lowest fortification level, are 0.00020 $\mu g/cm^2$ and 0.00002 $\mu g/cm^2$.

Several types of quality control data were generated in this study. These include a pre-field method validation study, a storage stability study, concurrent laboratory controls, and concurrent fortified recovery samples. In the pre-field method validation study, 1 control and 4 fortified recovery samples were analyzed (i.e., Report Tables 1 and 2). Chlorothalonil samples were fortified at levels ranging from 0.02 μg to 10.0 μg while HCB samples were fortified at levels ranging from 0.002 μg to 1.0 μg. Method validation recoveries for chlorothalonil and HCB respectively, were 98.8 percent (CV 8.88) and 87.8 percent (CV 13.5). A separate storage stability study which is reviewed in a separate deliverable to OREB was referenced in the report (i.e., Ricerca, Inc. Document Number 5224-92-0107-CR-001). According to the FDR study report, "samples stored at -16°C had 98 percent of the chlorothalonil and 85 percent of the HCB recovered after 21 days" and samples stored at 3°C had 100 percent of the chlorothalonil and 60 percent of the HCB recovered after 21 days." For each set of field samples the following samples were generated/analyzed concurrently with each batch of FDR samples collected in the field :

- chlorothalonil fortified dislodging solution with field control leaf disc wash (Report Table 3),

- chlorothalonil fortified dislodging solution without field control leaf disc wash (Report Table 4),

- HCB fortified dislodging solution with field control leaf disc wash (Report Table 5),

- HCB fortified dislodging solution without field control leaf disc wash (Report Table 6), and

- blank dislodging solution (Report Table 7).

Chlorothalonil and HCB recoveries are summarized below as well as the analysis of the blank samples described above. Mean chlorothalonil recovery from surfactant solution with the field control leaf disc wash was 92.7 percent (Report Table 3, N=11, CV 11.85). Mean chlorothalonil recovery from surfactant solution without field control leaf disc wash was 94.8 percent (Report Table 4, N=10, CV 8.26). Mean HCB recovery from surfactant solution with the field control leaf disc wash was 85.1 percent (Report Table 5, N=11, CV 16.86). Mean HCB recovery from surfactant solution without field control leaf disc wash was 88.1 percent (Report Table 4, N=11, CV 11.86). No detectable chlorothalonil or HCB residues were found in the any reagent blank sample analyzed concurrently with the field samples (Report Table 7). The data in Report Table 8 indicated that a total of 17 field control samples contained measurable levels of either chlorothalonil (N=13) or HCB residues (N=4). All control residues were at or near the LOQ except for 5 of the chlorothalonil samples and 1 of the HCB samples. Chlorothalonil contamination ranged up to 0.0042 $\mu g/cm^2$ while HCB contamination ranged up to 0.00032 $\mu g/cm^2$.

The results of the study indicate that the half-life for chlorothalonil FDRs on broccoli foliage is 3.6 days using a pseudo-first order kinetics model (i.e., semilog plot and $t_{1/2}=0.693/K_1$). Additionally, the results of the study indicate that the half-life for HCB FDRs on broccoli foliage is 10.3 days using a pseudo-first order kinetics model (i.e., semilog plot and $t_{1/2}=0.693/K_1$). An extensive statistical analysis of the available data in this study were completed by the investigators that indicated chlorothalonil dissipation correlated with the cumulative rainfall at the study site and did not correlate well with time after application (i.e., 8.92 inches total and ~0.25 inches on Day 0). The FDR data generated in this study were summarized by Versar as indicated in Attachment A of this review. The data included in Attachment A have been corrected for recovery as appropriate. Attachment A includes a semilog regression analysis of the data, a calculation of half-life using the pseudo first-order reaction kinetics model, and a presentation of the equations derived from the analysis.

Compliance with Sections 132 of Subdivision K of the Pesticide Assessment Guidelines (U.S. EPA, 1984) is critical. The itemized checklist lists below describes compliance with the major technical aspects of Subdivision K and is based on the "Checklist for Residue Dissipation Data" used for study reviews by the U.S. EPA/OPP/OREB. Additional data gaps identified in the study not covered in the scope of the checklist are also presented below on an individual basis.

- *Typical end-use product of the active ingredient used.* This criterion was met as Bravo 720, a liquid formulation containing 6.0 lb/gallon of the broad spectrum fungicide chlorothalonil (54.0 % a.i.) was used to make all applications in the study. However, as a supplement, additional information should be provided pertaining to the chemical nature of the formulation (e.g., category--EC or Soluble Liquid).

- *Site(s) tested representative of reasonable worst-case climatic conditions expected in intended use areas.* This criterion was not met. The study was conducted in Madison, Ohio which is located in northeastern Ohio. California is the largest single producing broccoli state. Additionally, California is typically considered a worst case scenario for FDR data generation. However, broccoli production in California was not addressed in this study. The northeastern part of Ohio in which this study was conducted would be anticipated to be cooler and more humid than most major broccoli producing states (e.g., Florida, Arizona, and California) as it is located close to Lake Erie. No environmental fate data were provided in the report to justify the selection of this particular geographic area for the study (e.g., hydrolytic or photolytic potential not described) as opposed to more arid regions (e.g., other areas in California or Arizona) or the more humid environment of Florida.

- *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.* This criterion was partially met. The study was completed using an application method that is typical of the large-scale agricultural production of broccoli and other truck vegetable crops. All applications were completed by applying 26 to 34 gallons per acre which is approximately 25 to 50 percent higher than the minimum dilution allowable by

the Bravo 720 label for dilute sprays (i.e., 20 to 150 gallons per acre is allowable). The rate used in the study for six of the eight applications was 1.5 pints of Bravo 720 per acre (i.e., 1.125 lb ai/acre) while the other two remaining applications were completed at an application rate of 1.11 pints of Bravo 720 per acre (i.e., 0.8325 lb ai/acre). The maximum application rate allowable per the label for broccoli is 2 pints of Bravo 720 per acre in California (i.e., 1.5 lb ai/acre). The Bravo 720 label indicates that applications can be completed "at 7 to 10 day intervals or as necessary to maintain control" of the intended pest throughout the growing season. The application regimen for this study included 8 distinct Bravo 720 applications at roughly the intervals specified by the label.

- *Application(s) occurred at time of season that the end-use product is normally applied to achieve intended pest control.* This criterion was not met. No thorough discussion regarding the common agricultural practices associated with broccoli cultivation and chlorothalonil use was included in the report. Particularly, no discussion of broccoli cultural practices in the northeast region of Ohio was provided along with documentation concerning the differences between this region and the major broccoli producing regions such as California and Florida.

- *Meteorological conditions including temperature, wind speed, daily rainfall and humidity provided for the duration of the study.* This criterion was met. All required data were presented in the study records.

- *Reported residue dissipation data in conjunction with toxicity data must be sufficient to support the determination of a reentry interval.* This criterion was not met. No toxicity data were provided and the FDR phase of the study.

- *Residue storage stability, method efficiency (residue recovery), and limit of quantification provided.* This criterion was met for all chlorothalonil and HCB residue analyses. Several types of analytical quality control data were collected/generated in this study for both chlorothalonil and HCB residues. These data included a pre-field method validation study, a separate storage stability (reviewed in separate document), concurrent laboratory reagent blanks and field control samples, and concurrent laboratory fortified samples using surfactant

solution and surfactant solution that had been used to wash field control samples. The separate storage stability study will be reviewed in a separate document. All FDR samples were collected in the field, transported to the nearby analytical laboratory, dislodged at the laboratory, and extracted on the sample collection day (i.e., aqueous surfactant solutions were partitioned with an organic solvent). As a result, the only sample storage was for the extracts which were stored until analysis (i.e., any degradation during this interval would be addressed by the concurrent laboratory recovery samples). For the method validation study and for all concurrent laboratory recovery scenarios (e.g., chlorothalonil with surfactant solution only), the recoveries averaged greater than 85 percent. The limit of quantification for both chlorothalonil and HCB was based on the lowest fortification levels analyzed. The fortification levels used by Versar for all calculations for chlorothalonil and HCB respectively, were 0.00020 $\mu g/cm^2$ and 0.00002 $\mu g/cm^2$.

- *Duplicate foliar and/or soil samples collected at each collection period.* This criterion was met. Triplicate treated field FDR samples and 5 control samples were collected during each monitoring interval.

- *Control and baseline foliar or soil samples collected.* This criterion was partially met. Prior to the last of eight applications samples were collected from the plot to be treated. Additionally, samples from a control plot were collected concurrently during each subsequent sample collection interval. A total of 8 applications were made in this study. No samples apparently were collected prior to the initial application or after each application in order to determine if the chlorothalonil and HCB levels prior to and after the final application were reasonable (i.e., this is critical as ~ 0.25" of rainfall was noted on the day of the final application -- see below).

- *Sufficient collection times to establish dissipation curve. First sample time taken as soon as sprays dry or dusts settle. Short durations should exist between earlier sample intervals and may lengthen with later samples.* This criterion was not met. A series of eight Bravo 720 applications were completed in this study. Samples were not collected prior to and after each application in order to assess the accumulation of chlorothalonil and HCB residues over time between each application. The sample collection intervals appear appropriate as the data show significant dissipation throughout the study interval to levels approximately equivalent to the level of quantification.

- *Foliar residue data expressed as µg or mg/cm² leaf surface area.* This criterion was met. All FDR data were reported as µg/cm² of leaf surface area.

- *Soil residue data expressed as µg/g of fine soil material.* This criterion is not applicable to this study as no soil samples were collected.

As described above, pertinent data gaps critical to the scientific validity and regulatory acceptability (i.e., Subdivision K compliance) of the study, not addressed above, are presented below. The following issues were identified:

- A significant rainfall (~0.25 inches) was noted on the date of the final Bravo 720 application. Additionally, during the kinetics phase of the study (i.e., interval from final application through Day 36 -- 7/8/92 to 8/13/92), a total of 8.92 inches of rainfall was monitored on the treated plot. No explanation was provided in the report regarding the impacts of these weather events or why an additional Bravo 720 application was made to the treated broccoli in order to assess dissipation kinetics with a more typical cumulative rainfall.

- The GLP/Quality Assurance Statement included in the report presented a series of inspection dates but did not include a description of the types of inspections that were completed (i.e., it was impossible to ascertain what aspects of the study were inspected).

- Several field control samples contained measurable quantities of chlorothalonil and HCB residues which were attributed to laboratory contamination. It is not clear if cross-contamination could have potentially occurred during the sample collection process or if there are other plausible explanations for these measured levels.

To summarize, the broccoli foliar dislodgeable residue study completed in support of the regulatory requirements for chlorothalonil did not meet the criteria contained in Subdivision K of the Pesticide Assessment Guidelines. This assessment is based on several major issues including the following: (1) the study was conducted in Ohio which is not a major broccoli producing region of the United States, (2) the study was not conducted at the maximum labelled application rate for broccoli -- the label stipulates that 2.0 pints Bravo 720 per acre can be used while 1.5 pints per acre or less was the rate for all applications, (3) a significant rainfall event occurred on the day of the final application (i.e., the initiation of the kinetics phase of the study), (4) almost 9 inches of rainfall was monitored during the conduct of the study, and (5) FDR samples were not collected during the multiple application process in order to assess the potential accumulation of chlorothalonil and HCB residues over time due to multiple applications.

CHERRY STUDY REVIEW

Chlorothalonil and HCB (hexachlorobenzene -- a manufacturing impurity) foliar dislodgeable residues were collected from treated cherry trees after a series of Bravo 720 applications. The field portion of the study was conducted at the Ricerca, Inc. experimental farm located in Concord, Ohio and the analytical portion of the study was conducted at the Ricerca, Inc. laboratory facility in Painesville, Ohio. The field study was initiated on May 4, 1992 and was conducted through July 13, 1992. Treated and control plots were used in this study. "A block of 4 year old sour cherry trees (Prunus cerasus cv. 'Mont-morency') was used." The treated plot consisted of "five adjacent trees within a single row. A second row of five trees was used as the control plot and was isolated from the treated plot to deter contamination from spray drift." The number of trees per acre in the treated orchard was 182 based on a row spacing of 16 feet on center and in-row spacing of trees at 15 feet on center. According to the study report, "all sour cherry trees in the orchard were maintained according to standard commercial practices." In this study, a total of four Bravo 720 applications were made using an airblast sprayer at the following cherry growth stages: early white bud (4/29/92), full bloom (5/6/92), petal fall (5/14/92), and shuck split (5/27/92). Each application was made at a rate of 4.125 pints/acre (i.e., 3.1 lb ai/acre) in approximately 102 gallons per acre. A Durland-Wayland Model AF 100-28 Airblast Sprayer mounted on a John Deere 2040 tractor was used to make all applications. The sprayer was equipped with 6 typical Spraying Systems Tee Jet Nozzles (i.e., 5 D4s & 1 D2 with 23 or 25 whirl plates) oriented on one side of the sprayer. Other sprayer parameters were similar between each of the 4 applications (i.e., 150 psi, 1.3 to 1.4 mph, 2 feet from target crop, and 2.1 to 2.3 gallons output per minute).

Foliar dislodgeable residue samples were collected on Day 0 (i.e., day of final application) and at 1, 2, 5, 8, 15, 22, 29, 36, and 43 days after the final application. Five control and triplicate treated foliar dislodgeable residue (FDR) samples were collected from the control and treated plots at each sample interval. Three control replicates were analyzed as field control samples while the remaining two samples were reserved for concurrent laboratory analysis purposes. Each FDR sample contained 40 leaf disc punches collected using a Birkestrand 1.262cm diameter leaf punch (i.e., each sample represented a double-sided surface area of $100cm^2$). Leaf disc samples were collected from the "3 inner trees of the row from both the control and treated plots, each tree constituting a replicate sample." The additional control sample replicates were collected randomly from each of the 3 designated inner control trees. All leaf disc samples were collected "randomly from the entire tree canopy." Between

replicates, the leaf punch device was washed with soapy water, rinsed with plain water, rinsed with acetone, and allowed to air dry. After sampling, the jars were sealed with Teflon-lined lids and placed on "Blue ice" for shipment to the analytical laboratory where the samples were dislodged on the sample collection day and subsequently analyzed.

FDR samples were dislodged at the analytical laboratory by shaking in two sequential 100 mL aliquots of an aqueous surfactant solution prepared by adding 100 mL of water and 0.4 mL of a surfactant solution (i.e., 1:50 v:v dilution of Aerosol OT 75) to the glass jars containing the leaf disc samples and shaking them on a reciprocating shaker for approximately 10 minutes. This procedure was repeated and both 100 mL aliquots of surfactant solution were added to separatory funnels. After the dislodging procedures were complete, a 50 mL aliquot of pet ether was used to rinse the glass jars for quantitative transfer into the separatory funnels along with a 10 mL aliquot of an aqueous NaCl solution (20 % w:v). After the partition, the organic layer was collected, concentrated, and solvent exchanged then passed through a Florisil clean-up column. Chlorothalonil and HCB residues were then quantified using a gas chromatograph equipped with an electron capture detector and a DB-5 capillary column. The LOQ for chlorothalonil and HCB respectively, based on recovery at the lowest fortification level, are 0.00020 $\mu g/cm^2$ and 0.00002 $\mu g/cm^2$.

Several types of quality control data were generated in this study. These include a pre-field method validation study, a storage stability study, concurrent laboratory controls, and concurrent fortified recovery samples. In the pre-field method validation study 1 control and 4 fortified recovery samples were analyzed (i.e., Report Tables 1 and 2). Chlorothalonil samples were fortified at levels ranging from 0.02 μg to 10.0 μg while HCB samples were fortified at levels ranging from 0.002 μg to 1.0 μg. Recoveries for chlorothalonil and HCB respectively, were 98.8 percent (CV 8.88) and 87.8 percent (CV 13.5). A separate storage stability study which is reviewed in a separate deliverable to OREB was referenced in the report (i.e., Ricerca, Inc. Document Number 5224-92-0107-CR-001). According to the FDR study report, "samples stored at -16°C had 98 percent of the chlorothalonil and 85 percent of the HCB recovered after 21 days" and samples stored at 3°C had 100 percent of the chlorothalonil and 60 percent of the HCB recovered after 21 days." For each set of field samples the following samples were generated/analyzed concurrently with each batch of FDR samples collected in the field :

- chlorothalonil fortified dislodging solution with field control leaf disc wash (Report Table 3),

- chlorothalonil fortified dislodging solution without field control leaf disc wash (Report Table 4),

- HCB fortified dislodging solution with field control leaf disc wash (Report Table 5),

- HCB fortified dislodging solution without field control leaf disc wash (Report Table 6), and

- blank dislodging solution (Report Table 7).

Chlorothalonil and HCB recovery are summarized below as well as the analysis of the reagent and field blank samples described above. Mean chlorothalonil recovery from surfactant solution with the field control leaf disc wash was 90.9 percent (Report Table 3, N=20, CV 13.76). Mean chlorothalonil recovery from surfactant solution without field control leaf disc wash was 90.8 percent (Report Table 4, N=20, CV 17.61). Mean HCB recovery from surfactant solution with the field control leaf disc wash was 92.1 percent (Report Table 5, N=18, CV 20.61). Mean HCB recovery from surfactant solution without field control leaf disc wash was 92.2 percent (Report Table 4, N=18, CV 22.00). Chlorothalonil residues at the LOQ were measured in 2 reagent blank samples while no detectable HCB residues were found in the any reagent blank sample analyzed concurrently with the field samples (Report Table 7). The data in Report Table 8 indicated that a total of 10 field control samples contained measurable levels of either chlorothalonil (N=9) or HCB residues (N=1). All control residues were at or near the LOQ except for 2 of the chlorothalonil samples, 1 contained a residue that was approximately 3.5 times higher than the LOQ and the other contained a chlorothalonil residue that was approximately 25 times higher than the LOQ.

The results of the study indicate that the half-life for chlorothalonil FDRs on cherry foliage is 3.4 days using a pseudo-first order kinetics model (i.e., semilog plot and $t_{1/2}=0.693/K_1$). Additionally, the results of the study indicate that the half-life for HCB FDRs on cherry foliage is 7.4 days using a pseudo-first order kinetics model (i.e., semilog plot and $t_{1/2}=0.693/K_1$). An extensive statistical analysis of the available data in this study were completed by the investigators that indicated chlorothalonil dissipation may directly correlate with the

cumulative rainfall at the study site. The FDR data generated in this study were summarized by Versar as indicated in Attachment B of this review. The data included in Attachment B have been corrected for recovery as appropriate. Attachment B includes a semilog regression analysis of the data, a calculation of half-life using the pseudo first-order reaction kinetics model, and a presentation of the equations derived from the analysis.

Compliance with Sections 132 of Subdivision K of the Pesticide Assessment Guidelines (U.S. EPA, 1984) is critical. The itemized checklist lists below describes compliance with the major technical aspects of Subdivision K and is based on the "Checklist for Residue Dissipation Data" used for study reviews by the U.S. EPA/OPP/OREB. Additional data gaps identified in the study not covered in the scope of the checklist are also presented below on an individual basis.

- *Typical end-use product of the active ingredient used.* This criterion was met as Bravo 720, a liquid formulation containing 6.0 lb/gallon of the broad spectrum fungicide chlorothalonil (54.0 % a.i.) was used to make all applications in the study. However, as a supplement, additional information should be provided pertaining to the chemical nature of the formulation (e.g., category--EC or Soluble Liquid).

- *Site(s) tested representative of reasonable worst-case climatic conditions expected in intended use areas.* This criterion was not met. The study was conducted in Concord, Ohio which is located in northeastern Ohio. Michigan is the largest producer of sour variety cherries while Washington state is the largest producer of sweet variety cherries according to *Agricultural Statistics 1989* (USDA). California, it should be noted, is also a large producer of sweet variety cherries. No discussion was provided in the report concerning how the Ohio site relates to the large cherry producing areas of the United States or generally why the site was selected (except for logistical ease). Additionally, California cannot be ignored in the site selection process as this region has distinctly different weather patterns and conditions compared to the other major cherry producing regions of the country (i.e., conditions in California may make reentry exposure more hazardous in this region than in the other regions -- arid regions are often considered the "worst-case" for reentry exposure).

- *Duplicate foliar and/or soil samples collected at each collection period.* This criterion was met. Triplicate treated field FDR samples and 5 control samples were collected during each monitoring interval.

- *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.* This criterion was partially met. The study was completed using an airblast sprayer which is the typical application method that used in the large-scale agricultural production of stone fruits such as cherries. All applications were completed by applying from 99.3 to 104 gallons per acre which is in the range of application volumes allowable by the Bravo 720 label but is not the lowest volume allowable per the label. The application volume range specified by the label ranges from 20 gallons per acre (sweet and tart cherries) up to 300 gallons per acre for tart cherries and 400 gallons per acre for sweet cherries. The Bravo 720 application rate used for each of the four applications was 4.125 pints per acre (i.e., 3.1 lb ai/acre). However, cherries can be treated for brown rot blosson blight at up to 5.5 pints per acre (i.e., 4.125 lb ai/acre) if the trees are higher than 20 feet (i.e., at the following growth stages: popcorn or early white bud, full bloom, and petal fall). The higher rate applies to 3 of the 4 applications completed in this study (i.e., the only application for which the higher rate is not applicable would be the final one at the shuck-split stage).

- *Application(s) occurred at time of season that the end-use product is normally applied to achieve intended pest control.* This criterion was not met. No thorough discussion regarding the common agricultural practices associated with cherry cultivation and chlorothalonil use was included in the report. Particularly, no discussion of cherry cultural practices in the northeast region of Ohio was provided along with documentation concerning the differences between this region and the major cherry producing regions such as Michigan.

- *Meteorological conditions including temperature, wind speed, daily rainfall and humidity provided for the duration of the study.* This criterion was met. All required data were presented in the study records.

- *Reported residue dissipation data in conjunction with toxicity data must be sufficient to support the determination of a reentry interval.* This criterion was not met. No toxicity data were provided and the FDR phase of the study.

- *Residue storage stability, method efficiency (residue recovery), and limit of quantification provided.* This criterion was met for all chlorothalonil and HCB residue analyses. Several types of analytical quality control data were collected/generated in this study for both chlorothalonil and HCB residues. These data included a pre-field method validation study, a separate storage stability (reviewed in separate document), concurrent laboratory reagent blanks and field control samples, and concurrent laboratory fortified samples using surfactant solution and surfactant solution that had been used to wash field control samples. The separate storage stability study will be reviewed in a separate document. All FDR samples were collected in the field, transported to the nearby analytical laboratory, dislodged at the laboratory, and extracted on the sample collection day (i.e., aqueous surfactant solutions were partitioned with an organic solvent). As a result, the only sample storage was for the extracts which were stored until analysis (i.e., any degradation during this interval would be addressed by the concurrent laboratory recovery samples). For the method validation study and for all concurrent laboratory recovery scenarios (e.g., chlorothalonil with surfactant solution only), the recoveries averaged greater than 90 percent. The limit of quantification for both chlorothalonil and HCB was based on the lowest fortification levels analyzed. The fortification levels used by Versar for all calculations for chlorothalonil and HCB respectively, were 0.00020 $\mu g/cm^2$ and 0.00002 $\mu g/cm^2$.

- *Control and baseline foliar or soil samples collected.* This criterion was partially met. Prior to the last of four applications, samples were collected from the plot to be treated. Additionally, samples from a control plot were collected concurrently during each subsequent sample collection interval. A total of 4 applications were made in this study. No samples apparently were collected prior to the initial application or after each application in order to determine if the chlorothalonil and HCB levels prior to and after the final application were reasonable.

- *Sufficient collection times to establish dissipation curve. First sample time taken as soon as sprays dry or dusts settle. Short durations should exist between earlier sample intervals and may lengthen with later samples.* This criterion was partially met. A series of four Bravo 720 applications were completed in this study. Samples were not collected prior to and after each application in order to assess the accumulation of chlorothalonil and HCB residues over time between each application. The sample collection intervals during the kinetics aspect of the study appear appropriate as the data show significant dissipation throughout the study interval to levels approximately equivalent to the level of quantification.

- *Foliar residue data expressed as μg or mg/cm² leaf surface area.* This criterion was met. All FDR data were reported as $\mu g/cm^2$ of leaf surface area.

- *Soil residue data expressed as μg/g of fine soil material.* This criterion is not applicable to this study as no soil samples were collected.

As described above, pertinent data gaps critical to the scientific validity and regulatory acceptability (i.e., Subdivision K compliance) of the study, not addressed above, are presented below. The following issues were identified:

- The GLP/Quality Assurance Statement included in the report presented a series of inspection dates but did not include a description of the types of inspections that were completed (i.e., it was impossible to ascertain what aspects of the study were inspected).

- Several field control samples contained measurable quantities of chlorothalonil and HCB residues which were attributed to laboratory contamination. It is not clear if cross-contamination could have potentially occurred during the sample collection process or if there are other plausible explanations for these measured levels.

To summarize, the cherry foliar dislodgeable residue study completed in support of the regulatory requirements for chlorothalonil did not meet the criteria contained in Subdivision K of the Pesticide Assessment Guidelines. This assessment is based on several major issues including the following: (1) the study was conducted in Ohio which is not a major cherry producing region of the United States, (2) the study was not conducted at the maximum labelled application rate for cherries -- 3 of 4 of the study applications could have been completed at a rate that is 33 percent higher than the rate used in the study, and (3) FDR samples were not collected during the multiple application process in order to assess the potential accumulation of chlorothalonil and HCB residues over time due to multiple applications.

ATTACHMENT A
BROCCOLI KINETICS DATA

PPA SUPPORT TASK: 2994.101
VERSAR,INC. 7/1/95 JLD

LOQ SUMMARY	(ug/cm2)
CHLOROTHALONIL	0.00020
HCB	0.00002

REVIEW OF CHLOROTHALONIL BROCCOLI FOLIAR DISLODGEABLE RESIDUE DISSIPATION STUDY
DISSIPATION KINETICS CALCULATIONS:PSEUDO 1st ORDER ANALYSIS

PAI (DAYS)	RESIDUE LEVELS CHLORTHALONIL (ug/cm2)	HCB (ug/cm2)	Ln [RESIDUE LEVELS] CHLORTHALONIL (ug/cm2)	HCB (ug/cm2)
0	0.8470	0.00015	-0.1661	-8.8049
1	0.5830	0.00009	-0.5396	-9.3157
2	1.2100	0.00028	0.1906	-8.1807
5	0.7370	0.00016	-0.3052	-8.7403
8	0.3080	0.00007	-1.1777	-9.5670
15	0.4140	0.00013	-0.8819	-8.9480
22	0.3550	0.00011	-1.0356	-9.1150
29	0.0062	0.00001	-5.0832	-11.5129
36	0.0002	0.00001	-8.5172	-11.5129

LINEAR REGRESSION [LIN/LIN]		LINEAR REGRESSION [SEMILOG]	
CHLOROTHALONIL FDRs			
Regression Output:		Regression Output:	
Constant	0.82619824248	Constant	0.60939875085
Std Err of Y Est	0.2270045526	Std Err of Y Est	1.46667123701
R Squared	0.71057308191	R Squared	0.77848846085
No. of Observations	9	No. of Observations	9
Degrees of Freedom	7	Degrees of Freedom	7
Correlation Coefficient	0.84295497028	Correlation Coefficient	0.88231993112
X Coefficient(s)	-0.025215099	X Coefficient(s)	-0.19491797
Std Err of Coef.	0.0060824247	Std Err of Coef.	0.039298407
HCB FDRs			
Regression Output:		Regression Output:	
Constant	0.00017066909	Constant	-8.5823196155
Std Err of Y Est	6.7883805E-05	Std Err of Y Est	0.73970819771
R Squared	0.36584252379	R Squared	0.52640300951
No. of Observations	8	No. of Observations	8
Degrees of Freedom	6	Degrees of Freedom	6
Correlation Coefficient	0.60484917441	Correlation Coefficient	0.72553635988
X Coefficient(s)	-4.45552E-06	X Coefficient(s)	-0.06739045
Std Err of Coef.	2.394825E-06	Std Err of Coef.	0.026095646

HALF LIFE:DAYS (LIN/Ln)	
CHLOROTHALONIL	HCB
3.56	10.28

NOTES:

* ALL VALUES USED FOR CALCULATIONS ARE AVERAGES OF REPLICATE SAMPLE ANALYSES AT EACH INTERVAL. ONE HALF LOQ USED IF NO RESIDUES IDENTIFED.
* HALF LIVES CALCULATED USING PSEUDO 1st ORDER REACTION KINETICS MODEL [t1/2=0.693/Ka) WHERE Ka=X COEFFICIENT.
* ALL RESIDUE VALUES ARE AVERAGE LEVELS FOR EACH SAMPLE COLLECTION INTERVAL
* CHLOROTHALONIL RESIDUE LEVELS NOT CORRECTED FOR AVAILABLE QC RESULTS AS ALL AVERAGE RECOVERIES WERE >= 90%.
* HCB LEVELS CORRECTED FOR QC RESULTS AS AVERAGE RECOVERY FOR FORTIFIED LEAF DISC SOLUTIONS WAS = 85 %.
* PAI = POST APPLICATION INTERVAL

ATTACHMENT A
CHERRY KINETICS DATA

PPA SUPPORT TASK: 2994.101
VERSAR,INC. 7/1/95 JLD

LOQ SUMMARY	(ug/cm2)
CHLOROTHALONIL	0.00020
HCB	0.00002

REVIEW OF CHLOROTHALONIL CHERRY FOLIAR DISLODGEABLE RESIDUE DISSIPATION STUDY
DISSIPATION KINETICS CALCULATIONS:PSEUDO 1st ORDER ANALYSIS

PAI (DAYS)	RESIDUE LEVELS CHLORTHALONIL (ug/cm2)	RESIDUE LEVELS HCB (ug/cm2)	Ln [RESIDUE LEVELS] CHLORTHALONIL (ug/cm2)	Ln [RESIDUE LEVELS] HCB (ug/cm2)
0	1.3500	0.00028	0.3001	-8.1807
1	1.5600	0.00027	0.4447	-8.2171
2	1.2200	0.00018	0.1989	-8.6226
5	0.5630	0.00008	-0.5745	-9.4335
8	0.4720	0.00007	-0.7508	-9.5670
15	0.0927	0.00002	-2.3784	-10.8198
22	0.0241	0.00001	-3.7255	-11.5129
29	0.0057	0.00002	-5.1673	-10.8198
36	0.0004	0.00001	-7.8240	-11.5129
43	0.0004	0.00001	-7.8240	-11.5129

LINEAR REGRESSION [LIN/LIN]		LINEAR REGRESSION [SEMILOG]	
CHLOROTHALONIL FDRs			
Regression Output:		Regression Output:	
Constant	1.05965657131	Constant	0.59764256543
Std Err of Y Est	0.372272137	Std Err of Y Est	0.43319173362
R Squared	0.68294524617	R Squared	0.98425640931
No. of Observations	10	No. of Observations	10
Degrees of Freedom	8	Degrees of Freedom	8
Correlation Coefficient	0.8264050134	Correlation Coefficient	0.99209697576
X Coefficient(s)	-0.032970574	X Coefficient(s)	-0.20669147
Std Err of Coef.	0.0079424723	Std Err of Coef.	0.009242199
HCB FDRs			
Regression Output:		Regression Output:	
Constant	0.00019174385	Constant	-8.6283745818
Std Err of Y Est	7.1782567E-05	Std Err of Y Est	0.59187557361
R Squared	0.63127847771	R Squared	0.83232153082
No. of Observations	9	No. of Observations	9
Degrees of Freedom	7	Degrees of Freedom	7
Correlation Coefficient	0.7945303504	Correlation Coefficient	0.91231657379
X Coefficient(s)	-6.65842E-06	X Coefficient(s)	-0.09348211
Std Err of Coef.	1.923363E-06	Std Err of Coef.	0.015858883

HALF LIFE:DAYS (LIN/Ln)	
CHLOROTHALONIL	HCB
3.35	7.41

NOTES:

* ALL VALUES USED FOR CALCULATIONS ARE AVERAGES OF REPLICATE SAMPLE ANALYSES AT EACH INTERVAL. ONE HALF LOQ USED IF NO RESIDUES IDENTIFED.
* HALF LIVES CALCULATED USING PSEUDO 1st ORDER REACTION KINETICS MODEL [t1/2=0.693/Ka) WHERE Ka=X COEFFICIENT.
* ALL RESIDUE VALUES ARE AVERAGE LEVELS FOR EACH SAMPLE COLLECTION INTERVAL
* RESIDUE LEVELS NOT CORRECTED FOR AVAILABLE QC RESULTS AS ALL AVERAGE RECOVERIES WERE >= 90%.
* PAI = POST APPLICATION INTERVAL

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R132516

Chemical: Chlorothalonil

PC Code:
081901

HED File Code: *19050 Versar DER Warning: May not have been QAed by EPA--*
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