

IR-4 NATIONAL PESTICIDE CLEARANCE PROTOCOL  
CLETHODIM / RICE

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PR No.: 13184  
Date: Aug-23

**1. PROJECT TITLE:** CLETHODIM: Magnitude of the Residue on RICE

**2. JUSTIFICATION AND OBJECTIVES:**

IR-4 has received a request for the minor use of clethodim on rice for control of red rice.

To establish this tolerance, it is required that the magnitude of the residue in or on the commodity be determined as per EPA Series 860 Guidelines. The purpose of this study is to collect and analyze treated and untreated residue samples from appropriate field sites according to the application parameters requested to provide the sponsor with residue chemistry data to support a pesticide tolerance for regional use in California.

**3. SPONSOR/TESTING FACILITY NAME, ADDRESS AND PHONE:**

IR-4 Project Headquarters, North Carolina State University, 1730 Varsity Drive, Suite 210, Venture IV, Raleigh, NC 27606, Telephone #: (919) 515-1552

**4. STUDY DIRECTOR<sup>1</sup>:**

Cristina Marconi, IR-4 Headquarters, North Carolina State University, 1730 Varsity Dr, Suite 210, Venture IV, Raleigh, NC 27606, (919) 515-8723, Email: cmarche@ncsu.edu

**5. PROPOSED DATES:**

Experimental Start : 08/23  
Experimental Termination: 11/25  
Study Completion: 10/26

**6. STUDY DIRECTOR INITIALS:** CM

**7. STUDY AUTHORIZATION:**

|  |  |
|--|--|
|  8/25/23<br>Sponsor Representative / Date |  8/25/23<br>Cristina Marconi / Study Director / Date |
|--|--|

**8. GOOD LABORATORY PRACTICE COMPLIANCE:**

To determine the magnitude of residues of total clethodim in or on rice, this protocol will be employed using appropriate Standard Operating Procedures (SOP's) and will be conducted under provisions outlined in 40 CFR Part 160, in accordance with EPA's Good Laboratory Practice Standards. Canadian field/processing/analytical trials, if any, will be conducted at facilities consistent with the provisions outlined in the Organization for Economic Cooperation and Development (OECD) Series on Principles of Good Laboratory Practice and Compliance Monitoring.

The appropriate cooperative testing facility (field and laboratory) will be responsible for certifying that its portion of the study will be conducted in accordance with EPA's Good Laboratory Practice (GLP) Standards, 40 CFR 160, amended and effective Oct. 16, 1989. A statement of compliance, together with any GLP deviations will be signed and submitted by the appropriate Research Directors in their report or data package.

<sup>1</sup>In case the Study Director is not available, contact Dr. Jerry Baron at (908) 627-4213 or Dr. Deborah Carpenter at (215) 913-5931 for guidance.

**9. QUALITY ASSURANCE:**

Quality Assurance duties and responsibilities will be in conformance with 40 CFR 160.35. A Quality Assurance Statement will be submitted in the final report and shall include the date inspections were made and date(s) the findings were reported to the Study Director and management.

**10. TEST SYSTEM/CROP:**

Rice - Use a commercial variety. Report: variety, source, lot number, date received, planting date, and other descriptive information if available.

**11. TEST SYSTEM DESIGN and STATISTICAL METHOD:**

11.1 Each test site will consist of one untreated and one treated plot.

The individual plots shall be of adequate size to ensure that no more than 50% of the harvestable crop in the sampled area will be needed to provide the necessary plant material. See Parts 17 & 18 for requirements for residue sampling. The sampled crop must be commercially mature to be considered "harvestable", unless otherwise indicated in Part 15 or Part 17.

11.2 Employ adequate buffer zones between each of the plots to prevent contamination. For most application types, a minimum distance of 15 feet is required, but a minimum of 50 feet is strongly preferred. For applications made by airblast, mist blower, or power sprayers, a minimum distance of 50 feet is required, but a minimum of 100 feet is strongly preferred. When plants are used as a buffer between the untreated and treated plots, a lower distance is needed to prevent contamination, but the minimums indicated above must be observed. If another study using a test substance with the same active ingredient is being conducted at the same research site, the untreated plot from one study must be separated from the treated plot(s) of the other by the appropriate buffer zone indicated above.

11.3 If this pesticide use is not registered on this crop, federal law requires that the treated crop must be destroyed or handled in such a way that it is not consumed as a human food or animal feed.

11.4 **This section applies when a Field Research Director (FRD) has been assigned more than one trial in this study, or when two or more trials assigned to different FRDs are located within 18.6 miles (30 km) of each other. An independently prepared tank-mix must be used in each trial.**

Also, choose at least one option from below:

| Option | Description   |
|--------|---|
| A      | Trial sites must be separated by at least 30 km (18.6 miles) [measured as straight line distance]         |
| B      | Planting date (for annual crops) or first application date in each trial is separated by at least 30 days |

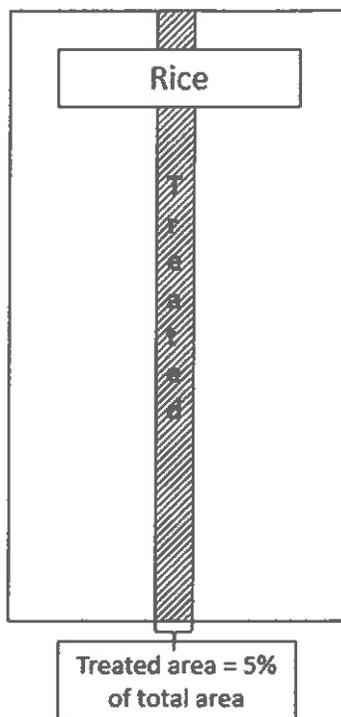
If these criteria cannot be met to separate multiple trials, the Field Research Director should contact the Study Director. Trials conducted in different calendar years are exempt from these requirements.

11.5 Mark plots with identifiable markers containing at minimum the Field ID number and treatment number or treatment name that will persist for the duration of the field research trial or that can be readily replaced. **Mark the treated area of the plot for taking phytotoxicity ratings and collecting samples.**

11.6 This study is not designed for statistical evaluation of field data.

11.7 Treated plot is to be designed in a way that approximately but no more than 5% of the field will be treated with clethodim and the samples will be collected within the treated band (if plants are available) and along both sides of the

treated band, as the crop on the treated area is expected to die with the application of clethodim. See suggestion of plot layout below:



#### **12. TEST SITE PREPARATION:**

Prepare or select a test site that has been maintained following good local agricultural practices for the production of rice including fertilization, irrigation, if necessary and available, and other practices that ensure commercially acceptable crop production.

The test site will have a known pesticide and fertilizer history of a minimum of 1 year and preferably 3 years.

#### **13. TEST/CONTROL SUBSTANCE:**

IR-4 Headquarters personnel will arrange procurement of GLP test substance from the registrant. The registrant will provide a copy of the Certificate of Analysis to IR-4 Headquarters.

Use Select Max® formulation (0.97 lbs active ingredient per gallon) of clethodim (EPA Reg. No. 59639-132, CAS# 99129-21-2) that has been characterized to meet GLP standards.

-Upon receipt, document the lot/batch number, condition, quantity received and if GLP characterized. Store the test substance in a secure, clean, dry area and document storage temperatures.

-Temperature monitoring should begin within 2 days of receipt of the test substance, regardless of where it is held or stored.

**Contact the Study Director** if there are any concerns regarding the GLP status, labeled identification, expiration date, etc. of the test substance.

EPA regulations require that test substance container(s) must be retained until the final study report is completed.

Study completion can be confirmed by contacting the Study Director or the Regional Field Coordinator, or by searching the IR-4 web site; click on "Food Crops" and under the "IR-4 Food Crops Database" click on the "Test Substance Container Disposal Approval" link. URL: <https://ir4app.cals.ncsu.edu/ir4foodpub/SubstanceDispoSch>

Alternatively, some registrants will archive the test substance containers. If test substance containers are shipped to another location, the shipment must be conducted in accordance with local, state, and Federal regulations. See shipping documents for directions for return of the test substance; if none are given, contact the registrant representative: Greg Clarke, Valent U.S.A. Corporation, (717) 502-1378, mobile: (717) 805-8322; E-mail: [Gregory.clarke@valent.com](mailto:Gregory.clarke@valent.com)

Before the completion of this study, the Study Director shall receive confirmation from the registrant of the location of a retention sample of the test substance. Control substances are not relevant to this study.

An optional tracking form that may be used to confirm that the correct test substance has been received (with the correct label and Certificate of Analysis) is available at: <https://ir4works.org/resources/frd-resources/>.

#### **14. TEST SUBSTANCE APPLICATION:**

**14.1 Simulate commercial application practices** by applying the test substance in a manner representative of an application technique that is used by area commercial growers, at the application rate and timing specified in Section 15.

- Use application equipment that will provide uniform application of the test substance and result in adequate canopy penetration and coverage.
- The test substance, if applied in a mixture, must be applied to the test system within 30 minutes of mixing, otherwise the mixture must be agitated just prior to making the application to ensure that it is well mixed. (The additional agitation should be documented in Part 6G of the Field Data Book.) The mixture must always be applied to the test system within 2 hours of mixing.
- Each field trial requires a unique spray mixture. Do not use the spray mixture from one field trial on another field trial.

**Contact the Study Director** if guidance is needed.

All study participants are **reminded** and **encouraged** to follow all appropriate campus, local, state (or provincial) and national regulations and laws in association with the safe use of pesticides.

**14.2 Full Calibrations for output and speed must be performed to ensure accurate delivery.**

A calibration consists of a minimum of 3 consecutive, documented checks for nozzle or hopper output and speed (equipment or walking speed). An output calibration is a 3 run discharge of all the nozzles. An output recheck is a single run discharge of all the nozzles. A speed calibration is 3 runs. A speed recheck is a single run. (When the output of an airblast sprayer is calibrated or rechecked, it is not necessary to record the outputs of individual nozzles.)

**Verification** of the actual amount of test substance **applied** will always be made using **the most recent complete calibration data for that equipment**. (Note: When the most recent calibration data is from another trial, a certified true copy of that data must be included in the field data book for this trial.)

#### **Discharge/Output Calibrations:**

Is this the first application of test substance in this trial?

**YES:** A full calibration is required just prior to the first application (allowable the day before the application, but calibration on the day of use is preferred). A single, full calibration may be used for multiple trials in the same study or multiple studies if the following conditions are met:

1. The first application in each trial is the day of the calibration or the following day.
2. Application parameters and equipment components remain the same for each of the trials.
3. A recheck is run in each of the trials after the first.

**NO:** A single run recheck may be conducted to confirm consistent delivery (within  $\pm 5\%$  of the last complete calibration) just prior to subsequent applications. (Full calibrations are preferred.)

**Recheck is required when:**

1. The equipment has been moved from the location where the most recent full calibration or recheck has occurred. (A sprayer that has been calibrated or rechecked at a farm or research station and then used to make an application somewhere else on that same farm or research station is *not* considered to have been "moved".)
2. The equipment has been cleaned.
3. Nozzles are removed and placed back on.
4. CO<sub>2</sub> tank has been changed.

**Recheck is not required when** the same Field Research Director is making applications on the same day for multiple trials in this study or separate studies, or multiple treatments in the same trial, unless there have been changes in other application parameters as described above.

**Full output calibration is required if:**

1. This is the first application in this trial
2. Application parameters or equipment components have changed (other than changing out CO<sub>2</sub> tanks) including:
  - a. Nozzle or hopper output
  - b. Nozzle size or type (full output calibration is not required if the same, clearly identified nozzles used for the full calibration have been placed back in the same positions on the boom after other nozzles have been used for another trial; in this case, only a recheck is needed)
  - c. Change in delivery pressure by more than 5% (even if it has been changed back to the pressure used during the initial calibration UNLESS the pressure change is accomplished by replacing the regulator, and the screw on the regulator used in this trial has not been turned since the full calibration)
3. A recheck is not within  $\pm 5\%$  of the last complete calibration.
4. The discharge of any single nozzle during a run of a full calibration or a recheck is greater than  $\pm 5\%$  of the mean of the same run (this does not apply to airblast sprayers). If this occurs the nozzle must be adjusted or replaced, and a full calibration must be conducted to ensure that the nozzle discharge is within 5% of the mean and to determine a new output.

**Target outputs:** The use of a target output rather than the mean output may be used in the calculations made prior to the application; however, a "target check" calibration consisting of three runs must be conducted just prior to each use of a target output, and the mean output must be within 5% of the target output. Using a target output rather than a mean output increases the probability that an application rate deviation will occur. Verification of the amount of test substance that has been applied in calculations that use the discharge rate will always be made using the most recent calibration data.

**Speed Calibrations:**

Conduct the speed calibration in an area adjacent to the test plot, or on similar terrain (allowed the day before the application, but calibration on the day of use is preferred).

Is this the first application of test substance in this trial?

**YES:** A full speed calibration is required.

Exceptions: 1) When a handgun is used to spray tree fruits or nuts, and each tree is sprayed for a predetermined time, a speed calibration is not required and 2) When applications are made in multiple trials on the same site, same day, using the same equipment and same speed, a speed calibration is only required for the first application made that day.

**NO:** A single run recheck may be conducted to confirm consistent speed ( $\pm 5\%$  of the last complete speed calibration or  $\pm 5\%$  of a target speed) just prior to subsequent applications.

**Full speed calibration is required when:**

1. A major equipment change has been made, such as from a tractor-pulled sprayer to a backpack sprayer.
2. A complete output calibration is performed.

**Speed recheck is required when:**

1. Speed calibration data from another trial is used, except for applications that are made on the same day on the same farm, using the same equipment and same speed.
2. Whenever an output recheck is performed, except for multiple applications within a study that are made on the same day on the same farm.

**Speed recheck is not required when** the same Field Research Director is making applications on the same day for multiple trials in this study, or multiple treatments in the same trial, unless there is a major equipment change or the treated plots are located on separate farms.

**14.3 Actual Application Rate:** Record actual application pass-times in the Field Data Book and verify the accuracy of the application against the protocol rate. **The application is considered acceptable if the accuracy is within -5% and +10% of the target rate specified in Section 15. If the application did not meet this range, the Study Director must be notified of this deviation before proceeding with this trial.**

The submitted Field Data Book shall contain the original calibration data or a true copy of all calibrations referenced, along with the original data from the rechecks performed for this trial.

#### 15. APPLICATION TREATMENTS AND TIMING:

| Trt# | Treatment | Target Rate of active ingredient | Target Rate of formulated product* | Application Type | Spray Volume Range** |
|------|-----------|----------------------------------|------------------------------------|------------------|----------------------|
| 01   | Untreated | Not Applicable                   | Not Applicable                     | Not Applicable   | Not Applicable       |
| 02   | Clethodim | 0.121 lb ai/acre                 | 473 ml/acre + adjuvant***          | Banded           | 5-40 GPA             |

\*The nominal concentration of the formulated test substance will be used in calculating application rates (see Section 13 for the nominal concentration).

\*\*GPA=gallons per acre

\*\*\*All applications shall include a **crop oil concentrate (COC) at a rate of 1% v/v or nonionic surfactant (NIS) at a rate of 0.25% v/v.** Include a copy of the adjuvant label in the Field Data Book.

**Make one banded application to approximately but no more than 5% of the field at 50 ( $\pm 5$ ) days before harvest. The banded application should be made as a strip along the center of the plot to approximately but no more than 5% of the total area (see section 11.7).**

**Note:** At time of application, the rice field must be drained. Flooding cannot begin until a minimum of 48 hours after the spray solution has dried.

It is expected that the rice plants in the treated area will show significant injury symptoms from the application since this herbicide targets rice. If possible, take one or more photographs and send them to the Study Director via email.

In all field trials conducted in the state of California, phytotoxicity data must be collected at 7-14 days after each application using a 0-4 scale and entered into Field Data Book 6P (available on the IR-4 website). The phytotoxicity data is to be taken and recorded from three (3) different areas, the sprayed area where the application occurred, the adjacent area starting from the last senescent plant take rating at 0-6 inches from the edge of the application and at 6-12 inches from the edge of the application. Record damage to the foliage and stem. A follow-up rating is needed 7-14 days after the first evaluation, record if the width of the injured plants increased.

#### 16. SUPPLEMENTAL CROP TREATMENTS:

Protect the integrity of the field trial by managing pests that may cause significant damage to the test crop. Use only maintenance pesticides that have been registered on this commodity by EPA or the corresponding agency in the country in which the trial is located. Apply according to labeled directions. Make identical applications to the untreated and treated plots. In a field trial with multiple sample collection dates for the treated plot, maintenance applications may be made on the treated plot that are not made on the untreated plot or other plots from which sample collection has been completed.

Consult with Study Director if no registered pesticides are available to control the pests. Document all supplemental crop treatments. DO NOT USE pesticides that are similar to the test substance or other chemicals that might interfere with analysis of the test substance. If unsure, contact the Study Director.

#### 17. RESIDUE SAMPLE COLLECTION:

##### **Grain and Straw Samples:**

**Untreated plot:** Collect two samples, each sample should be representative of the entire plot (except plot ends). At 50 ( $\pm 5$ ) days after the last application, harvest rice in a manner simulating commercial practices. For each sample, collect the rice (panicles and straw) from at least 12 separate areas of the plot (cut at approximately 15 cm above the ground). Each sample should be collected by making separate runs through the entire untreated plot.

**Treated plot:** At 50 ( $\pm 5$ ) days after the last application, harvest rice in a manner simulating commercial practices. For each sample, collect the rice (panicles and straw) from at least 12 separate areas within the target sampling areas (cut at approximately 15 cm above the ground). Collect 2 sets of samples (each set contains 2 samples), the first set of samples should be collected from the treated area where application was made (if rice grains are present), and/or within 1 foot of the edge of the treated area (on both sides of the treated sprayed area where rice plants with full grain formation are present). Collect the second set of samples from 2-3 feet from the edge of the treated area.

Start with the untreated plot or utilize separate personnel for the treated and untreated plots. Harvest of rice should simulate commercial practices. Each sample should be collected by making separate runs through the targeted sections of the plot, and should be representative of the section it is being collected from. Avoid collecting from the plot ends.

**For all samples:** Thresh the rice with a thresher or by hand to separate the grain (kernel and hull) and the straw. Collect duplicate grain samples weighing a minimum of 2 lb (but preferably not more than 3 lb). And collect duplicate straw samples weighing a minimum of 1 lb (but preferably not more than 2 lb). Do not use threshing equipment that could contaminate the grain sample with the straw sample.

Follow proper handling practices with clean or gloved hands and clean tools to prevent transfer of pesticide residue from one sample to another. If practical, complete harvest and sample preparation for the untreated plot(s) before proceeding to the treated plot(s).

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Place all samples in plastic-lined cloth bags. Bags may be obtained from the Regional Field Coordinator (Section 23). Identify each sample bag\*\* with correct Field ID number, Test Substance (chemical name listed in Section 15), complete sample ID (see Section 18.1) and harvest/sampling dates. After residue sample collection, store samples in a freezer. If the samples cannot be placed into a freezer within one hour, use an appropriate method of cooling and temperature-monitoring samples in order to maintain integrity.

\*\*When using IR-4 plastic lined cloth residue sample bags, complete attached sample tag as follows:  
**Field ID Number; Crop Fraction; Test Substance** (enter the chemical name listed in Section 15); **Sample ID; Trt#; Harvest Date; Sample Date; Field Research Director** (enter name and telephone number).

**18. FIELD RESIDUE SAMPLE INVENTORY:**

| SAMPLE ID | TRT# | TREATMENT                          | DAYS AFTER LAST APPLIC. | MINIMUM SAMPLE SIZE | CROP FRACTION |
|-----------|------|------------------------------------|-------------------------|---------------------|---------------|
| GA        | 01   | Untreated                          | NA                      | 2 lb.               | Grain         |
| GB        | 01   | Untreated                          | NA                      | 2 lb.               | Grain         |
| GC        | 02   | Clethodim 0-1 ft from sprayed area | 50(±5)                  | 2 lb.               | Grain         |
| GD        | 02   | Clethodim 0-1 ft from sprayed area | 50(±5)                  | 2 lb.               | Grain         |
| GE        | 02   | Clethodim 2-3 ft from sprayed area | 50(±5)                  | 2 lb.               | Grain         |
| GF        | 02   | Clethodim 2-3 ft from sprayed area | 50(±5)                  | 2 lb.               | Grain         |
| SA        | 01   | Untreated                          | NA                      | 1 lb.               | Straw         |
| SB        | 01   | Untreated                          | NA                      | 1 lb.               | Straw         |
| SC        | 02   | Clethodim 0-1 ft from sprayed area | 50(±5)                  | 1 lb.               | Straw         |
| SD        | 02   | Clethodim 0-1 ft from sprayed area | 50(±5)                  | 1 lb.               | Straw         |
| SE        | 02   | Clethodim 2-3 ft from sprayed area | 50(±5)                  | 1 lb.               | Straw         |
| SF        | 02   | Clethodim 2-3 ft from sprayed area | 50(±5)                  | 1 lb.               | Straw         |

**19. RESIDUE SAMPLE HANDLING AND SHIPMENT:**

Sample handling and storage methods can be outlined generally in SOP's, but describe methods fully in the Field Data Book.

For pre-shipment storage, the samples will be held frozen at temperatures generally less than -18 °C (0 °F), allowing for normal variations of less than 24 hours' duration due to freezer cycling, sample movement, etc. If the analytical laboratory is close enough to the field site to permit delivery of the samples by field personnel on the day of sampling, then pre-shipment frozen storage is not required.

**Freezer logs** will be used to document all sample additions to and removals from storage. All on-site storage temperatures will be monitored and documented.

**For express shipments (overnight carriers such as Federal Express or Airborne), contact the designated person (noted below) from the analytical laboratory prior to sample shipment for any specific shipping instructions. For shipments via freezer truck (ACDS), it is acceptable to contact the laboratory prior to shipment, on the day of**

**shipment, or on the day after the samples have been loaded on the truck.** Shipment of frozen samples will be by freezer truck or express shipment, unless the samples are brought to the analytical laboratory by field trial personnel. Shipments sent via express shipment (overnight carriers such as Federal Express or Airborne) will require the addition of quantities of dry ice sufficient to maintain sample integrity while in transit to the laboratory (see IR-4 Advisory 2007-01 for more information). If field trial personnel transport the samples to the analytical laboratory directly from the plots and the sampling-to-freezer interval is more than one hour, an appropriate method of cooling and temperature-monitoring shall be used to maintain sample integrity. If the samples are stored frozen at the field trial facility prior to being transferred to the analytical laboratory by field trial personnel, then appropriate methods must be used to keep the samples frozen during transport. These methods should be documented in the Field Data Book.

Document the notification made to the sample destination by use of e-mail, telephone log, Field Data Book communication note, etc.

**Insert a true copy of Field Data Book Part 8B and a blank copy of Field Data Book Part 8C (Sample Arrival Check Sheet) into each box or container used to ship sample bags. This documentation is needed even when field personnel transport the samples to the analytical laboratory.**

**For analysis, send samples to:** Bronson Hung, IR-4 Western Region Laboratory, Center for Health and the Environment (CHE), Univ of California, Davis, Building 3792, 1250 Old Davis Road, Room 129, Davis, CA 95616-8615, PH: (530) 752-4742; e-mail: bkhung@ucdavis.edu

## **20. FIELD DOCUMENTATION AND RECORD KEEPING:**

All operations, data and observations appropriate to this study should be recorded directly and promptly into the IR-4 Field Data Book.

The content of the Field Data Book should be sufficiently detailed to completely reconstruct the field trial. At a minimum, collect and maintain the following raw data:

- 20.01- Names of all personnel conducting specific research functions
- 20.02- Amendments and deviations from protocol relevant to this trial and standard operating procedures (including copies of signed protocol changes received prior to submission of the Field Data Book to the Regional Field Coordinator).
- 20.03- Test site information
- 20.04- Plot maps
- 20.05- Test substance receipt, use and container/substance disposition records
- 20.06- Test substance storage conditions (including temperatures)
- 20.07- Data regarding calibration and use of application equipment
- 20.08- Treatment application data
- 20.09- Crop maintenance pesticides and cultural practices, test plot history, and soil information. (Reporting soil information from typical farm service soil analysis labs, or past history for the farm, or from official documents, such as the SCS Soil Survey for the test plot area is adequate for this study. The nature of this study is such that soil characteristics do not need to be determined under GLP standards.)
- 20.10- Residue sample identification, collection, storage conditions and handling (Weight measurements are considered estimates for the samples collected from field or processing trials, and the scales/balances used for this purpose do not need to be maintained in strict adherence to GLP.)

- 20.11- Residue sample shipping information
- 20.12- Description of crop destruction, or explanation for lack of destruction
- 20.13- Daily Meteorological/Irrigation records--required from the date of planting or transplanting of annual crops or for a minimum of one month prior to the first application onto perennial crops, until last residue sample collection. These records do not need to be determined under GLP standards. If the protocol requires that transplants are treated with the test substance prior to transplanting, then weather records are required from the date of seeding. If transplants are used for an IR-4 trial but no test substance applications are made prior to the transplanting, then temperature/humidity records are NOT required for the period prior to transplanting.
- 20.14- Pass times (if applicable) and other data to confirm amount of material applied to plots
- 20.15- Equipment maintenance records with indication of routine vs. non-routine nature of maintenance
- 20.16- Other applicable data requested in the IR-4 Field Data Book necessary for confirmation that the study was conducted in accordance with the protocol.

Compliance with GLPS is not required for the collection of data associated with crop phytotoxicity under Part 6K, but may be considered in compliance with GLPS if Part 6P is used.

#### **21. PROTOCOL/SOP MODIFICATIONS - FIELD RESEARCH:**

**Consult with the Study Director** and with the Regional/ARS Field Coordinator to discuss desired changes in the protocol **prior to occurrence**. If appropriate, an amendment will be issued.

Any deviations from the protocol will require the Field Research Director to complete a written report outlining the changes. **Provide this report to the Study Director promptly** (e.g. within 14 days of occurrence or recognition) for review and signature.

All deviations from the approved SOP's also require documentation and **approval by the Study Director**.

#### **22. FIELD RESEARCH REPORT/ARCHIVING:**

The Field Research Director will forward the completed **originals** of the IR-4 Field Data Book and other raw data to the Regional/ARS Field Coordinator as soon as possible after the shipment of residue samples.

The Field Research Director will maintain a complete certified true copy of these field documents.

The original IR-4 Field Data Book and other raw data will be forwarded to IR-4 Headquarters for reporting and archiving.

**23. FIELD PERSONNEL / ID NO. / REGIONAL/ARS FIELD RESEARCH LOCATION**

Field trials will be conducted at the appropriate sites to support the establishment/maintenance of a regional residue tolerance for California. If a Field Research Director is assigned more than one trial in this study, refer to Section 11.4 for requirements to differentiate the trials.

| <b>Field Research Director</b>  | <b>Field ID NO.</b> | <b>RFC</b> | <b>Test Crop</b> |
|---|---------------------|------------|------------------|
| Seth Watkins, <u>MAILING</u> : Seth Watkins, Dept of Plant Sciences, MS 4, University of California, 1 Shields Ave., Davis, CA 95616; Cell: 530-312-8339; e-mail: swatkins@ucdavis.edu and <u>SHIPPING</u> : Seth Watkins, Dept of Plant Sciences, 1210 PES University of California, One Shields Ave, Davis, CA 95616; Cell#: 530-312-8339; e-mail: swatkins@ucdavis.edu | 13184.23-CA29       | WSR        | Rice             |
| Seth Watkins, <u>MAILING</u> : Seth Watkins, Dept of Plant Sciences, MS 4, University of California, 1 Shields Ave., Davis, CA 95616; Cell: 530-312-8339; e-mail: swatkins@ucdavis.edu and <u>SHIPPING</u> : Seth Watkins, Dept of Plant Sciences, 1210 PES University of California, One Shields Ave, Davis, CA 95616; Cell#: 530-312-8339; e-mail: swatkins@ucdavis.edu | 13184.23-CA30       | WSR        | Rice             |

**RFC = Regional/ARS Field Coordinator**

**Location:**

**ARS:** Dr. Alvin Simmons, USDA-ARS, US Vegetable Laboratory, 2700 Savannah Highway, Charleston, SC 29414; Tel: (843) 402-5307; e-mail: Alvin.simmons@usda.gov

**NER:** Ms. Marylee Ross, University of Maryland, LESREC, 27664 Nanticoke Rd., Salisbury, MD 21801; Tel: (410) 742-8788 x 310; e-mail: mross@umd.edu

**NCR:** Nicole Soldan, IR-4 North Central Research Center, Michigan State University, 1066 Bogue St. Plant and Soil Sciences Building – Rm A440, Michigan State University, East Lansing, MI 48824; Cell: 517 712-8441; Email: schroe65@msu.edu;

**SOR:** Dr. Janine Spies, Univ of Florida, 1642 SW 23<sup>rd</sup> Drive, Bldg 685, PO Box 110720, Gainesville, FL 32611-0720, Ph: 352-294-3991; e-mail: jrazze@ufl.edu

**WSR:** Dr. Kari Arnold, Regional Field Coordinator, Western Region IR-4 Project, 4218 Meyer Hall, University of California-Davis, Davis, CA 95616 (530) 752-7634; Cell: (530) 574-9181; e-mail: klamold@ucdavis.edu

**CANADA:** Christine Gagnon, (Mailing) Agriculture & Agri-Food Canada, Pest Management Centre, Building 57, CEF, 960 Carling Avenue, Ottawa, ON Canada K1A 0C6, Cell: (343) 550-1047; e-mail: christine.gagnon2@agr.gc.ca (Shipping): GLP Admin, Agriculture & Agri-Food Canada, Pest Management Centre, Building 57, CEF, 960 Carling Avenue, Ottawa, ON Canada K1A 0C6; Tel: 613-759-6625; e-mail: aafc.glpadmin-adminbpl.aac@agr.gc.ca

**24. LABORATORY PERSONNEL/ID NO.:**

**LAB ID NO.: 13184.23-CAR04**

**LABORATORY RESEARCH DIRECTOR/TESTING LABORATORY:**

Dr. Matt Hengel, University of California, Davis, Western Region IR-4 Project, 4218 Meyer Hall, Davis, CA 95616, (530) 752-2402, Cell#: 530-867-2402; e-mail: mjhengel@ucdavis.edu

**25. LABORATORY SAMPLE INVENTORY:**

Treated and untreated samples of rice will be received from each of the trial sites in Section 23.

Notify appropriate Field Research Director and Regional/ARS Field Coordinator of sample receipt.

#### 26. LABORATORY SAMPLE IDENTIFICATION:

Each sample (raw commodity, crop fractions, storage stability, method validation, etc.) is to be assigned a unique laboratory sample number by the laboratory personnel.

A cross-reference must be maintained between the assigned laboratory sample number and the identification utilized in the Residue Sample Shipping and Identification Sheet.

#### 27. LABORATORY SAMPLE STORAGE/PREPARATION:

Store samples in a limited access area at temperatures generally less than -18 °C (0 °F), allowing for normal variations of less than 24 hours' duration due to freezer cycling, sample movement, etc., that will maintain frozen sample integrity, until extraction.

The samples may be stored whole or ground, depending on the standard procedure of the analytical laboratory. However, if maceration will cause residue deterioration, then samples must be stored whole until analysis.

Do not composite samples.

The entire sample provided from the field must be ground. If sample is too large to be manageable then contact the Study Director for appropriate subsampling to assure the representative nature of the sample obtained in the field is maintained by the laboratory procedure.

Generally, sample extracts should be stored at  $\leq 4^{\circ}\text{C}$  for no longer than 14 days before analysis.

Storage stability of extracts must be demonstrated if extracts are not analyzed on the same day as they are obtained.

Concurrent fortifications may be used to show extract storage stability, as long as the extracts from the concurrent fortifications have been stored at least as long as the extracts obtained from the weathered samples.

Contact the Study Director if samples extracts are stored greater than 14 days prior to analysis.

All storage temperatures, conditions and location of sample storage are to be monitored and documented.

#### 28. LABORATORY REFERENCE SUBSTANCE:

Obtain the laboratory reference substance(s), Clethodim Sulfoxide (CSO), Clethodim Sulfone (CSO<sub>2</sub>), and 5-hydroxy Clethodim Sulfone (5-OH CSO<sub>2</sub>) from Valent, Contact Greg Clarke, Valent U.S.A. Corporation, (717) 502-1378, mobile: (717) 805-8322; E-mail: Gregory.clarke@valent.com to procure the proper material.

Document the date the analytical standards are received, the source, stated purity, storage conditions, and expiration date.

Use only reference standards that have been characterized to meet GLP standards.

Archival and characterization of the reference substance (purity, identity, stability and solubility) is the responsibility of the registrant.

#### 29. ANALYTICAL METHODOLOGY:

##### REFERENCE METHOD:

"Determination of Clethodim Residues in Crops, Chicken and Beef Tissues, Milk, and Eggs." Analytical Method # RM-26B-3, 1994, Valent U.S.A. Corporation.

#### REFERENCE METHOD MODIFICATIONS/METHOD VALIDATION

The above listed Reference Method(s) may be modified if needed for the test matrix.

The Reference Method, along with any modifications must be validated on each crop fraction prior to residue sample analysis of that crop fraction.

To validate the method, fortify some of the control samples in triplicate with clethodim sulfoxide (CSO) and 5-hydroxy clethodim sulfone (5-OH CSO<sub>2</sub>) at a minimum of 2 concentration levels, lowest level of method validation (0.01 ppm or lower), and 0.1 ppm.

A minimum of 6 fortification samples (recovery spikes) at the lowest level of method validation (LLMV) is required for each analyte on each fraction prior to completion of the analytical phase of the study. **The acceptable recovery range is 70-120%.**

**Documented approval from the Study Director** is needed for recoveries outside of this range.

Document the exact procedures for sample analysis.

This validated step-by-step Working Method should incorporate all changes from the Reference Method.

**Provide the Study Director** with a copy of this Working Method and results of method validation prior to treated sample analysis.

If the Working Method has been used successfully on the test matrix or a similar matrix, the Study Director may waive the requirement for method validation. **Contact the Study Director for details.**

#### SAMPLE ANALYSIS:

Samples will be analyzed for the total and/or combined residues of clethodim sulfone and 5-hydroxy clethodim sulfone following the Working Method. Results will be reported as clethodim equivalents.

For each field trial associated with this study, analyze at least one untreated and all treated residue samples for each matrix.

**Contact the Study Director** if residues above the lowest level of method validation for each matrix are detected in the untreated samples.

Any changes or modifications to the Working Method **require Study Director approval.** Whenever possible, **notify the Study Director** prior to occurrence.

Any change or modification to the Working Method must be documented in the raw data and discussed in the final report.

A typical analytical set (or run) should consist of calibration standards, untreated sample(s), concurrent recovery sample(s), and treated sample(s). Each analytical set must begin and end with a calibration standard. Additional calibration standards should be injected with sample analysis to ensure goodness of fit to the standard curve.

Over the course of method validation, residue sample and storage stability (if appropriate) analysis, adequate fortification samples that bracket the actual residues should be analyzed. At least one concurrent fortification sample should be analyzed per analytical set.

**The Study Director should be immediately notified** if concurrent recoveries deviate from the acceptable recovery range of 70% to 120%.

All efforts will be made to resolve existing recovery problems before continuing forward with additional analytical sets.

If residues in samples are above the highest Working Method validation concentration, additional recovery samples at levels above actual residues must be run in triplicate (3 uniquely extracted samples) as soon as practical. A minimum of 6 fortification samples (recovery spikes) at the lowest level of method validation (LLMV) is required for each analyte on each fraction prior to completion of the analytical phase of the study.

Treated samples may be analyzed using a screening run prior to analysis of treated samples using the working method, if the procedure is covered in the laboratory SOPs and the working method for the study. The peak areas of the treated samples and highest standard from any screening run will not be quantified or reported. (Any data, such as chromatograms, generated during screening run(s) will be kept.)

#### STORAGE STABILITY ANALYSIS:

Storage stability samples shall not be fortified until after the working method has been successfully validated. Once the method is validated, a minimum of nine subsamples of a control from each crop fraction shall be fortified with clethodim sulfoxide (CSO) and 5-hydroxy clethodim sulfone (5-OH CSO<sub>2</sub>) at 0.1 ppm each. Three fortified subsamples must be analyzed on the day of fortification to document the residues in the 0-day storage stability sample. If it is anticipated that the lab will not be able to analyze the study samples within a year after receipt of the last field sample from the study, consult with the study director prior to spiking the storage stability samples to determine whether more than nine subsamples will be spiked for storage stability analyses. For storage of samples longer than a year, analyses of additional intervals may be required.

Sufficient storage stability data for clethodim covering the storage of samples for 343 days has been reported by the registrant. Storage stability analyses of clethodim will be run only if sample storage exceeds the aforementioned storage period(s) reported by the registrant.

**Contact the Study Director to determine if Storage Stability Samples need to be analyzed.**

If storage stability analyses will be required, discuss with the study director what storage stability intervals will be analyzed. Only if directed by the Study Director, three samples of each analyte and crop fraction will be analyzed at each analysis interval and after the appropriate storage period. The analysis of the final interval of storage stability samples may be conducted following a storage period equal to or greater than 90% of the longest storage period of the field – treated samples from collection in the field/processing facility until their analysis. The remaining samples will be retained for long-term storage.

If analysis of treated/control samples is completed within 30 days of harvest analysis of storage fortification samples may not be required. If appropriate, **contact Study Director**.

#### STATISTICAL METHOD(S):

Utilize regression analysis to determine the linearity of the standard curve ( $r^2$ ) or the goodness of fit if the standard curve is non-linear.

Criteria for acceptance of the standard curve(s) or other statistical methods shall be determined by Laboratory Research Director and documented in the raw data.

**30. DISPOSITION OF SAMPLES:**

A minimum of 100 g or all (if less than 100 g) of each of the remaining frozen treated and untreated crop samples is to be retained for at least 12 months after submission of the laboratory report.

Long term fortified storage study samples shall be retained for a period of 1 to 5 years, as appropriate, after submission of the final report.

Sample extracts can be disposed of after data analysis.

The Study Director is to be contacted prior to discarding samples.

**31. LABORATORY PROTOCOL/SOP MODIFICATIONS - LABORATORY RESEARCH:**

Consult with the Study Director regarding desired changes in the protocol prior to occurrence. If appropriate, an amendment will be issued. Any unauthorized changes to the protocol will require the Laboratory Research Director to complete a written report outlining the changes.

This report should be provided to the Study Director promptly (e.g. within 14 days of occurrence) for review and signature.

All deviations from the approved SOP's also require documentation and approval by the Study Director.

**32. LABORATORY DOCUMENTATION AND RECORD KEEPING:**

All operations, data and observations shall be recorded in the analyst's notebook and log books, which must be signed and dated on date of entry.

At a minimum, collect and maintain the following raw data:

- 32.01 - Analytical standard(s) receipt, use and disposition records
- 32.02 - Analytical standard(s) storage conditions
- 32.03 - Analytical standard(s) dilution calculations and preparation records
- 32.04 - Sample storage conditions and locations
- 32.05 - Calculation work sheets
- 32.06 - All chromatograms, including those that are not reported
- 32.07 - Chain of custody records
- 32.08 - Deviations from protocol, Working Method and/or standard operating procedures
- 32.09 - Name of personnel conducting specific research functions
- 32.10 - Sample analysis worksheets
- 32.11- Storage stability fortification records
- 32.12 - Concurrent recovery fortification records

A study file shall be developed and maintained by the Laboratory Research Director in conjunction with the analysis. It will contain a copy of the protocol, all pertinent raw data, documentation, records, correspondence, and the final analytical summary report. In addition, records of equipment maintenance and calibrations will be kept and periodically archived.

### 33. LABORATORY RESEARCH REPORT:

The analytical summary report sent to IR-4 HQ shall contain, but not be limited to:

- 33.01 - Applicable method validation data
- 33.02 - Applicable storage stability data
- 33.03 - Residue levels for control samples, treated samples, and concurrent fortified recoveries
- 33.04 - Complete copy of the analytical Working Method
- 33.05 - Any modifications or deviations from the protocol and/or Working Method
- 33.06 - A minimum of 10 representative chromatograms of treated samples (if fewer than 10 submit all), a minimum of three chromatograms each of control and fortified control samples, chromatograms (one of each concentration) for at least one set of calibration standards for each compound analyzed, and any chromatograms of samples with unusual or inconsistent results
- 33.07 - Summary of quantitative data associated with samples and spike recovery samples should be provided (e.g. peak heights, injection volumes, sample sizes, final volumes, etc.)
- 33.08 - Clearly presented example calculations or statistical evaluations
- 33.09 - Discussion of results (including purpose of method modifications, sample storage conditions, etc.)
- 33.10 - Summary data associated with calibration standards (dilution and use records, calibration curves, etc.)

### 34. LABORATORY ARCHIVES:

**For studies assigned to the IR-4 Laboratory at the University of California (CAR), or University of Florida (FLR):** When the final analytical summary report is completed and sent to the sponsor representative, all original raw data including a "true copy" of the final analytical summary report shall be secured in the archives of the Laboratory Research Director/Testing Facility.

**For studies assigned to any other analytical laboratory:** When the final analytical summary report is completed the analytical report and all original raw data will be sent to IR-4 Project Headquarters, **1730 Varsity Drive, Suite 210, Venture IV, Raleigh, NC 27606** (when an original document cannot be provided a "true copy" will be provided). All original raw data shall be secured in the archives of IR-4 Headquarters. A "true copy" of the raw data and the final analytical report shall be secured in the archives of the Laboratory Research Director/Testing Facility.

**IR-4  
FIELD DATA BOOK**

**TITLE: CLETHODIM MAGNITUDE OF THE  
RESIDUE ON RICE**

**PR# 13184**

**SPONSOR**

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