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

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

10/25/2000

MEMORANDUM

OFFICE OF
PREVENTION, PESTICIDES AND
TOXIC SUBSTANCES

SUBJECT: PP# 0E06097. Clethodim (ANSI) in/on Root Vegetables (except Sugar Beet) Crop Subgroup 1b, Leaves of Root and Tuber Vegetables (except Sugar Beet) Crop Group 2, Leaf Petioles Crop Subgroup 4b, Melon Crop Subgroup 9a, Squash/cucumber Crop Subgroup 9b, Cranberry, Strawberry, and Clover. Evaluation of Analytical Method and Magnitude of the Residue Data.

DP Barcodes: D263055 PRAT Case Nos:
Submission Nos: S531616 & S556745
PC Code: 121011 Caswell#: 721F
Trade Name: Select® Herbicide EPA Reg#: 59639-78
Select® 2EC Herbicide EPA Reg#: 59639-3
Class: Herbicide 40 CFR: §180.458
MRID Nos: 45027802, 45027803, 45027804, 45027805, 45027806, 45027807, 45027808, 45027809 and 44753203.

FROM: Manying Xue, Chemist
Registration Action Branch 3
Health Effects Division (7509C)

THRU: Stephen Dapson, Branch Senior Scientist
Registration Action Branch 3
Health Effects Division (7509C)
10/25/2000

TO: Joanne Miller, PM Team # 23
Registration Division (7505C)

The Interregional Research Project No. 4 (IR-4), on behalf of the Agricultural Experiment Stations of various states, has submitted a petition for the establishment of permanent tolerances for residues of the herbicide clethodim (Select® Herbicide 0.94EC (also called Prism) and Select® 2EC Herbicide (EPA Reg. Nos 59639-78 and 59639-3)). The proposed tolerances for the combined residues of clethodim [(E)-(±)-2-[1-[[(3-chloro-2-propenyl)oxy]imino]propyl]-5-[2-(ethylthio)propyl]-3-hydroxy-2-cyclohexen-1-one] and its metabolites containing the 5-(2-(ethylthiopropyl)cyclohexene-3-one and 5-[2-(ethylthio)propyl]-5-hydroxycyclohexene-3-one moieties and their sulphoxides and sulphones for the raw agriculture commodities are as follows:

Root Vegetables Except Sugar Beets (Subgroup 1B)	1.0 ppm
Leaves of Root and Tuber Vegetables, exc. sugar beets (Group 2)	2.0 ppm
Leaf Petioles (Subgroup 4B)	0.5 ppm
Melon (Subgroup 9A)	2.0 ppm
Squash/Cucumber (Subgroup 9B)	0.5 ppm
Cranberry	0.5 ppm
Strawberry	5.0 ppm
Clover, forage	10.0 ppm
Clover, hay	20.0 ppm

Clethodim (SELECT® 2 EC, EPA Reg. No. 59639-3; SELECT® or PRISM® Herbicide, EPA Reg. No. 59639-78; and SELECT SUPER® Herbicide, EPA Reg. No. 59639-102) is currently registered for post-emergence control of annual and perennial grasses in alfalfa, cotton, dry beans, peanuts, onions, dry bulb onions, soybeans, sugar beets, and tomatoes. The petitioner is proposing the use of PRISM® Herbicide (EPA Reg. No. 59639-78), a 0.94 lb/gal EC, on the crops listed above.

Permanent tolerances have been established under 40 CFR §180.458(a)(1), (4), and (5) for the combined residues of the herbicide clethodim and its metabolites containing the 2-cyclohexen-1-one moiety in/on the fat, meat, and mbyp of cattle, goats, hogs, horses, poultry, and sheep at 0.20 ppm, milk at 0.05 ppm, eggs at 0.20 ppm, cottonseed at 1.0 ppm, potatoes at 0.5, soybeans at 10.0 ppm, potato flakes and granules at 1.0 ppm, cottonseed meal at 2.0 ppm, and soybean soapstock at 15.0 ppm. In addition, permanent tolerances are established under 40 CFR §180.458(a)(3) and (6) for the combined residues of clethodim and its metabolites containing the 5-(2-ethylthiopropyl)cyclohexene-3-one and 5-(2-ethylthiopropyl)-5-hydroxycyclohexene-3-one moieties and their sulphoxides and sulphones, expressed as clethodim, in/on dry bulb onions at 0.20 ppm, sugar beet roots at 0.20 ppm, sugar beet tops at 0.50 ppm, and sugar beet molasses at 2.0 ppm.

Time limited tolerances (set to expire on 4/30/01) are established under 40 CFR §180.458(a)(2) for the combined residues of clethodim and its metabolites containing the 5-(2-ethylthiopropyl)cyclohexene-3-one and 5-(2-ethylthiopropyl)-5-hydroxycyclohexene-3-one moieties and their sulphoxides and sulphones, expressed as clethodim, in/on alfalfa forage at 6 ppm, alfalfa hay at 10 ppm, dry beans at 2 ppm, peanuts and peanut hay at 3 ppm, peanut meal at 5 ppm, tomatoes at 1 ppm, tomato paste at 3 ppm, and tomato puree at 2 ppm. Tolerances have also been proposed for residues in/on tuberous and corm vegetables, sunflowers, and canola (PP#7F4873).

Residue chemistry data associated with this petition were reviewed by the Dynamac Corporation. The data assessment has undergone secondary review within RAB3 and has been revised to reflect current HED and OPP policies.

The chemical structure for clethodim is given below:

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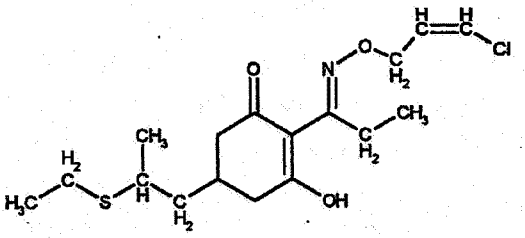

CONCLUSIONS

OPPTS 830 Series GLNs: Product Properties

1. The product chemistry data for clethodim were previously submitted. The manufacturing process of technical grade active ingredient (TGAI) and the formulations were reviewed (PP#9F3743, M. Nelson, 3/12/90). No deficiencies and no toxicological concerns for any clethodim impurities were cited.

OPPTS GLN 860.1200: Proposed Uses

2. The proposed use directions for carrots and radish (the root vegetables except sugar beets, crop subgroup 1b), radish top (the leaves of root and tuber vegetables, group 2), celery (the leaf petioles, crop subgroup 4b), cantaloupes (the melon, crop subgroup 9a), summer squash and cucumbers (the squash/cucumber, crop subgroup 9b), clover, cranberries, and strawberries are adequate.

OPPTS GLN 860.1300: Nature of the Residue - Plants

3a. No new plant metabolism study has been submitted with this petition. Metabolism studies for clethodim in/on carrots, soybeans, and cotton were previously reviewed (PP#9F3743, MRIDs 41030137 & 41030138, M. Nelson, 3/12/90). The qualitative nature of the clethodim residue in plants is adequately understood for root crops and oil seed crops. HED prevously concluded that the residues of concern are clethodim and its metabolites containing the 2-cyclohexen-1-one moiety. However, the residues of concern are now described as clethodim and metabolites containing the 5-(2-(ethylthiopropyl)cyclohexene-3-one and 5-(2-(ethylthiopropyl)-5-hydroxycyclohexene-3-one moieties and their sulphoxides and sulphones in order to harmonize with the Codex MRL (PP#4F4340, D203378, J. Morales, 1/31/95).

3b. For future petitions on crops other than root crops and oil seed crops, additional metabolism data may be required.

OPPTS GLN 860.1300: Nature of the Residue - Livestock

4. Metabolism studies of [propyl-1-^{14}C]-clethodim in a lactating goat and laying hens were previously reviewed (PP#9F3743, MRID# 41030139 & 41030140, M. Nelson, 3/12/90). The nature of the residue in ruminants and poultry is adequately understood for the purposes of the subject petition. HED prevously concluded that the residues of concern are clethodim and its metabolites containing the 2-cyclohexen-1-one moiety.

OPPTS GLN 860.1340: Analytical Methods - Plants

5a. Method RM-26B-2 was validated for the analyses of residues of clethodim in/on radish, carrots, cucumbers, cranberries, and strawberries. The fortification levels were 0.14 ppm and 0.25 ppm for radish, 0.09 ppm - 0.23 ppm for carrots, 0.09 ppm - 1.2 ppm for cucumbers, 0.05 ppm - 1.0 ppm for cranberries, and 0.05 ppm - 20 ppm for strawberries. Average recoveries for all commodities were within the acceptable range for all fortification levels tested. The method RM-26B-2 for the determination of clethodim and its metabolites in radish, carrots cucumbers, cranberries, and strawberries is acceptable for data collection and enforcement purposes.

5b. Method RM-26B-3 (a modification of RM-26B-2) was validated for the analyses of residues of clethodim in/on celery, cantaloupes, and clover. The fortification levels were 0.5 ppm and 5.0 ppm for celery, 0.1 ppm - 5.0 ppm for cantaloupes, 0.5 ppm - 2.0 ppm for clover forage, and 0.2 ppm - 20 ppm for clover hay. Average recoveries for all commodities were within the acceptable range at all fortification levels tested. The method RM-26B-3 for the determination of clethodim and its metabolites in celery, cantaloupes, and clover is acceptable for data collection.

5c. The common moiety method RM-26B-3 for the determination of clethodim and its metabolites is similar to the common moiety method RM-26B-2. The method RM-26B-2 has previously undergone a successful Petition Method Validation by the Agency (PP#9F3734, MRID 41389901, M. Nelson, 5/4/90), and a confirmatory method, RM-26D-2 is also available. Both methods (RM-26B-2 & RM26D-2) have been forwarded to FDA as ecforcement methods for inclusion in PAM II.

OPPTS GLN 860.1340: Analytical Methods - Animals

6. Adequate analytical methodology is available to enforce tolerances for residues of clethodim and its metabolites in animal commodities. The Agency has concluded that the compound specific method, EPA-RM-26D-2, is suitable for enforcement of tolerances for total clethodim residues in crops and animal tissues, and it has been forwarded to FDA for publication in the Pesticide Analytical Manual, Volume II (PAM II).

OPPTS GLN 860.1360: Multiresidue Method

7. The petitioner has previously submitted data (1991; MRID 43166406, and 1992; MRID 43166407) describing the testing of clethodim and its metabolites through FDA Multiresidue Methods. These data, which have been forwarded to FDA for review, and indicate that adequate recoveries of clethodim, clethodim sulfoxide, and 5-OH clethodim sulfone have been obtained under FDA's multiresidue protocols (PP#9F3743, M. Nelson's memo of 3/12/90).

OPPTS GLN 860.1380: Storage Stability Data

8. The submitted storage stability data are adequate to support the residue field trials for carrots, radish, celery, cucumbers, summer squash, cantaloupes, clover, cranberries, and strawberries. The storage stability data showed that residues of clethodim and its metabolites are stable under frozen storage for 720 days (24 months) in carrots, 475 days (16 months) in radish, 739 days (24.6 months) in celery, 526 days (17.5 months) in cucumbers, 484 days (16 months) in summer squashes, 689 days (23 months) in cantaloupes, 309 days (10 months) in clover forage, 297 days (10 months) in clover hay, 673 days (22.4 months) in cranberries, and 810 days (27 months) in strawberries. Correction of the residue data for storage degradation is not required.

OPPTS GLN 860.1500: Crop Field Trials

9a. **The submitted carrot and radish field trial data and geographic representation for the root vegetables (except sugar beets)crop subgroup 1b are adequate to satisfy the requirements described in OPPTS 860.1500 for a tolerance.** Eight carrot field trials were conducted in CA (4), FL (1), MI (1), TX (1), and WA (1); and four radish trials were conducted in FL (1), MI (1), NY (1) and WA (1). Carrot samples were harvested 29-31 days following the last of two applications of clethodim (0.94 lb/gal EC) at 0.236-0.256 lb ai/A/application, at 14-15 day retreatment intervals (RTI), for a total of 0.480-0.512 lb ai/A/season (~1x the maximum proposed rate). Combined residues of clethodim ranged from <0.25 to <0.39 ppm. Radish root samples were harvested 14-15 days post-treatment following a single treatment with clethodim at 0.246-0.252 lb ai/A/season (1x rate). Combined residues were <0.45 ppm (<LOQ) in/on all radish samples. The submitted residue data indicate that the proposed 1.0 ppm tolerance for residues of clethodim and its metabolites in/on the root vegetables except sugar beets (crop subgroup 1b) is adequate.

9b. **The submitted radish top residue data and geographic representation for the leaves of root and tuber vegetables (excluding sugar beets) crop group 2 are adequate to satisfy the requirements described in OPPTS 860.1500 for a tolerance.** Four radish top trials were conducted in FL (1), MI (1), NY (1) and WA (1) following a single treatment with clethodim (0.94 lb/gal EC) at 0.25 lb ai/A/season (1x rate), and harvested 14-15 days post-treatment. Combined residues of clethodim were <0.46-<0.58 ppm in/on eight samples of

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radish tops. These data indicate that the proposed 2.0 ppm tolerance for residues of clethodim in/on the leaves of root and tuber vegetables (crop group 2, excluding sugar beets) is too high; the appropriate tolerance for residues of clethodim and its metabolites in/on the leaves of root and tuber vegetables (crop group 2, excluding sugar beets) should be 1.0 ppm. **Therefore, a revised Section F must be submitted proposing a tolerance at 1.0 ppm for residues of clethodim in/on the leaves of root and tuber vegetables.**

9c. **The submitted celery residue data and geographic representation for the leaf petioles crop subgroup 4b are adequate to satisfy the requirements described in OPPTS 860.1500 for a tolerance.** Five celery field trials were conducted in CA (2), FL (1), MI (1), and TX (1). Samples were harvested 29-31 days following the last of two applications at 0.24-0.29 lb ai/A/application, at 14- or 15-day RTIs, for a total seasonal rate of 0.49-0.57 lb ai/A (~1x the maximum proposed rate). Combined residues of clethodim were <0.40 - <0.53 ppm in/on celery. The proposed tolerance of 0.5 ppm for residues of clethodim in/on the leafy petioles (crop subgroup 4b) is not adequate; the appropriate tolerance for residues of clethodim and its metabolites in/on the leafy petioles (crop subgroup 4b) should be 0.6 ppm. **Therefore, a revised Section F must be submitted proposing a tolerance at 0.6 ppm for the leafy petioles crop subgroup 4b.**

9d. **The submitted cantaloupe residue data and geographic representation for the melon crop subgroup 9a are adequate to satisfy the requirements described in OPPTS 860.1500 for a tolerance.** Eight cantaloupe field trials were conducted in CA (3), FL (1), MI (1), SC (2), and TX (1). Samples were harvested 13-14 days (20 days, one test) following the last of two applications at 0.243-0.316 lb ai/A/application, at 12-14 day RTIs, for a total of 0.490-0.619 lb ai/A/season (~1x the maximum proposed rate). Combined residues of clethodim were <0.20-<1.3 ppm in/on cantaloupes. These data indicate that the proposed tolerance of 2.0 ppm for residues of clethodim and its metabolites in/on the melon crop subgroup is adequate.

9e. **The submitted squash (summer) and cucumber residue data and geographic representation for the squash/cucumber crop subgroup 9b are adequate to satisfy the requirement described in OPPTS 860.1500 for a tolerance.** Five summer squash field trials were conducted in NY (1), SC (1), FL (1), MI (1) and CA (1); and six cucumber field trials were conducted in FL (1), MI (1), NY (1), SC (1), TX (1) , and WI (1). Samples of summer squash were harvested 13 or 14 days following the last of two foliar applications of clethodim (0.94 lb/gal EC) at 0.237-0.256 lb ai/A/application, at 11-15 day RTIs, for a total seasonal rate of 0.478-0.507 lb ai/A (~1x the maximum proposed rate). Cucumber samples were harvested 13 or 14 days after two foliar applications of clethodim at 0.25 lb ai/A/application, at 12-14 day RTIs, totaling 0.50 lb ai/A (1x). Combined residues of clethodim were non-quantifiable (<LOQ; or <0.40 ppm) in/on all squash samples. Combined residues of clethodim were also non-quantifiable (<LOQ; or <0.27 ppm) in/on all cucumber samples. The submitted summer squash/cucumber residue data are adequate to support the proposed tolerance of 0.50 ppm for residues of clethodim and its metabolites in/on the

squash/cucumber crop subgroup 9b.

9f. **The submitted clover residue data and geographic representation are adequate to satisfy the requirements described in OPPTS 860.1500.** Three clover field trials were conducted in OR (3). Samples were harvested 15 days following a single application of clethodim (0.94 lb/gal EC) at 0.25 lb ai/A/season (1x the proposed maximum rate). Combined residues were <3.1-6.1 ppm in/on forage samples and 11.2-15.3 ppm in/on hay samples. These data indicate that the proposed tolerances with regional registration (limited to ID, OR, WA) for residues of clethodim and its metabolites in/on clover forage (10 ppm) and hay (20 ppm) are adequate.

9g. **The submitted cranberry residue data and geographic representation are adequate to satisfy the requirements described in OPPTS 860.1500.** Three cranberry field trials were conducted in MA (1), WI (1), and WA (1). Combined residues of clethodim were 0.12-0.32 ppm in/on cranberry samples harvested 29 or 30 days following the last of two applications of clethodim (0.94 lb/gal EC) at 0.241-0.277 lb ai/A/application, at 14-21 day RTIs, for a total of 0.492-0.516 lb ai/A/season (1x the maximum proposed rate). These data support the proposed tolerance of 0.5 ppm for residues of clethodim and its metabolites in/on cranberries.

9h. **The submitted strawberry residue data and geographic representation are adequate to satisfy the requirements described in OPPTS 860.1500.** Seven strawberry field trials were conducted in CA(2), FL (1), MI (1), NJ (1), NC (1), and WA (1). Combined residues of clethodim were 0.42-2.28 ppm in/on strawberry samples harvested 3-4 days after the last of two applications of clethodim (0.94 lb/gal EC) at 0.230-0.268 lb ai/A/application, at 13- or 14-day RTIs, for a total of 0.47-0.50 lb ai/A/season (~1x the maximum proposed rate). These data indicate that the proposed 5.0 ppm tolerance for residues of clethodim and its metabolites in/on strawberry is too high, and that a tolerance of 3.0 ppm would be appropriate. Therefore, **the petitioner must submit a revised Section F proposing a tolerance of 3.0 ppm for residues of clethodin in/on strawberries.**

OPPTS GLN 860:1520: Processed Food/Feed

10. There are no regulated processed food or feed items derived from the commodities associated with this petition; therefore, a discussion of tolerances for processed commodities is not relevant.

OPPTS GLN 860.1480: Meat/Milk/Poultry/Eggs

11a. The established tolerances on meat and milk are adequate to cover the proposed uses. According to Table 1 of OPPTS 860.1000 and the recommended and established tolerances for clethodim, the maximum theoretical dietary burdens were determined to be 14.41 ppm and 14.91 ppm for beef and dairy cattles, respectively. Based on the previous feeding studies, the secondary residues in meat and milk will not exceed the established

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tolerances.

11b. As there are no poultry feed items associated with the current petition, no secondary residues are expected to occur in poultry tissues and eggs.

OPPTS GLN 860.1850 and 860.1900: Confined/Field Accumulation in Rotational Crops

12. A confined rotational crop study of [ring-4,6-^{14}C]-clethodim with carrots, lettuce, and wheat (MRID 41030211) was conducted. The study was reviewed by E. B. Conerly (EFGWB Science Chapter for Clethodim, 06/26/1990). Results indicated that there is no need for field rotational crop trials. A 1- month plantback interval for crops rotated with alfalfa was specified (D 236382, M. Collantes, et. al, 2/10/98). The use directions submitted with the current petition do not specifically address rotational crops. The directions for use on fallow or nonproducing agricultural land state do not plant any crop for 30 days after application unless clethodim is registered for use on that crop.

International Harmonization of Tolerances

13. There are no established Codex maximum residue limits (MRLs) for residues of clethodim in/on the commodities discussed in the subject petition; therefore, there are no questions with respect to Codex/U.S. tolerance compatibility. Codex MRLs are currently established on various crop and livestock commodities in terms of the sum of clethodim and its metabolites containing 5-(2-ethylthiopropyl)cyclohexene-3-one and 5-(2-ethylthiopropyl)-5-hydroxycyclohexene-3-one moieties and their sulphoxides and sulphones, expressed as clethodim.

RECOMMENDATIONS

There are no residue chemistry data requirements that would preclude the establishment of permanent tolerances for residues of clethodim and its metabolites in/on the root vegetables except sugar beets (crop subgroup 1b), the melon (crop subgroup 9a), the squash/cucumber (crop subgroup 9b), clover, and cranberries.

Provided a revised Section F is submitted, as specified in Conclusions 9b, 9c & 9h, HED concludes that there are no residue chemistry data requirements that would preclude the establishment of permanent tolerances for residues of clethodim and its metabolites in/on the leaves of root and tuber vegetables (group 2), the leaf petioles (crop subgroup 4b), and strawberries.

HED recommends that the tolerances for the combined residues of clethodim [(E)-(±)-2-[1-[[(3-chloro-2-propenyl)oxy]imino]propyl]-5-[2-(ethylthio)propyl]-3-hydroxy-2-cyclohexen-1-one] and its metabolites containing the 5-(2-(ethylthiopropyl)cyclohexene-3-one and 5-(2-(ethylthiopropyl)-5-hydroxycyclohexene-3-one moieties and their sulphoxides and sulphones be

established as follows:

Vegetable, Root, Except Sugar Beet, Subgroup	1.0 ppm
Vegetable, Leaves of Root and Tuber, Except Sugar Beet, Group	1.0 ppm
Leaf Petioles Subgroup	0.6 ppm
Melon Subgroup	2.0 ppm
Squash/Cucumber Subgroup	0.50 ppm
Cranberry	0.50 ppm
Strawberry	3.0 ppm
Clover, forage	10.0 ppm
Clover, hay	20.0 ppm

HED will now initiate a Human Health Risk Assessment for these uses.

DETAILED CONSIDERATIONS

OPPTS 830 Series GLNs: Product Properties

The product chemistry data for clethodim were previously submitted. The manufacturing process of the technical grade active ingredient (TGAI) and the formulations were reviewed (PP#9F3743, M. Nelson, 3/12/90). No deficiencies and no toxicological concerns for any clethodim impurities were cited.

OPPTS GLN 860.1200: Proposed Uses

The petitioner has submitted a copy of the end-use product label for the 0.94 lb/gal EC of clethodim (PRISM® Herbicide; EPA Reg. No. 59639-78) together with supplemental label describing the amount, frequency, and timing of application of clethodim for the proposed uses.

The registered label states that applications may be made using ground or aerial equipment in a minimum of 5 or 3 gallons of water/A, respectively. Spot treatments may be made using hand sprayers or high-volume sprayers using hand guns with a ½-1% PRISM® Herbicide mix. The label specifies a maximum seasonal application rate of 0.5 lb ai/A (0.25 lb ai/A in Long Island, NY). The label prohibits application of clethodim through any type of irrigation system, and specifies a 12-hour restricted entry interval. Rotational crop restrictions are not specified with the exception of uses on fallow land which specify a 30-day PBI for crops without registered clethodim uses. The supplemental directions provided for each crop state that a crop oil concentrate containing at least 15% emulsifier should be used at 1% v/v of finished spray volume unless tank mix instructions indicate otherwise.

Root vegetables, except sugar beets (crop subgroup 1B). The proposed use allows up to two applications (one only for radish) at 0.25 lb ai/A/application with a minimum 14-day RTI; a 30-day preharvest interval (PHI;15-day PHI for radish) is proposed.

Leaves of root and tuber vegetables except sugar beet (crop group 2). The proposed use allows up to two applications (one only for radish and turnips) at 0.25 lb ai/A/application with a minimum 14-day RTI; a 30-day PHI (15 days for radish and turnips) is proposed.

Leaf petioles (crop subgroup 4B). The proposed use allows up to two applications at 0.25 lb ai/A/application with a minimum 14-day RTI; a 30-day PHI is proposed.

Melon and squash/cucumber (crop subgroups 9A and 9B). The proposed use allows up to two applications at 0.25 lb ai/A/application with a minimum14-day RTI; a 14-day PHI is proposed.

Strawberry. The proposed use allows up to two applications at 0.25 lb ai/A/application to strawberries with a minimum 14-day RTI; a 4-day PHI is proposed.

Cranberry. The proposed use allows up to two applications at 0.25 lb ai/A/application to cranberries with a minimum 14-day RTI; a 30-day PHI is proposed.

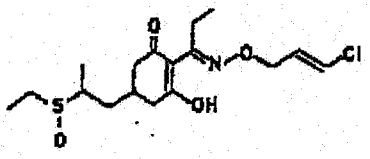
Clover (for seed production only). The proposed use allows a single application of clethodim at 0.25 lb ai/A to clover grown for seed; a 15-day PHI is proposed. Use is limited to ID, OR, and WA.

HED Comments/Conclusions:

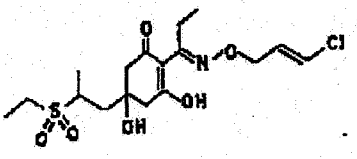
The proposed use directions for carrots and radish (the root vegetables except sugar beets crop subgroup 1b), radish top (the leaves of root and tuber vegetables, group 2), celery (the leaf petioles crop subgroup 4b), cantaloupes (the melon crop subgroup 9a), summer squash and cucumbers (the squash/cucumber crop subgroup 9b), clover, cranberries, and strawberries are adequate.

OPPTS GLN 860.1300: Nature of the Residue - Plants

No new plant metabolism study has been submitted with this petition. Metabolism studies for clethodim in/on carrots, soybeans, and cotton were submitted with PP#9F3743 (MRIDs 41030137 & 41030138) and discussed in the memo of 3/12/90 (M. Nelson). Immature carrots, soybeans, and cotton were treated twice at a 14-day interval with a 50:50 tautomeric mixture of ring [6-^{14}C]-clethodim at a rate equivalent to 0.25 lbs. ai/A as a postemergence foliar spray; grown to maturity in a greenhouse; and harvested with PHI's of 20, 30, and 70 days. The major metabolic pathways of clethodim (C) in plants are initial sulfoxidation to clethodim sulfoxide (CSO, structure shown below) followed by further oxidation to clethodim sulfone (CSO_2), elimination of the chloroallyloxy side chain to give the imine sulfoxide (ISO) and sulfone (ISO_2), and hydroxylation to form the 5-OH sulfoxide (5OH-SO) and sulfone (5OH-SO_2, structure shown below). Clethodim sulfoxide and clethodim sulfone conjugates were also detected as major or minor metabolites, depending on plant species and subfractions. Data are shown in Table 1. Also present as a minor metabolite was the aromatic sulfone. A study designed to follow the fate of the chloroallyloxy group was done side-by-side with the ^{14}C-ring-labeled clethodim study discussed above. The results showed that the chloroallyloxy moiety cleaved from clethodim underwent extensive metabolism, eliminating the chlorine atom and incorporating the three carbon moieties into natural plant components (with some being evolved as $^{14}CO_2$). Studies have been conducted only in a root crop (carrots) and two oilseeds (soybean and cotton) and it cannot be stated that the nature of the residue is understood in all plants. The residues of concern in Tuberous and Corm Vegetables (Crop Subgroup 1-C), sugar beets, sunflowers, canola, other root crops, and oil seed crops are clethodim and its metabolites containing the 5-(2-(ethylthiopropyl)cyclohexene-3-one and 5-(2-(ethylthiopropyl)-5-hydroxycyclohexene-3-one moieties and their sulphoxides and sulphones.



Clethodim sulfoxide



5-Hydroxy clethodim sulfone

Table. 1. Characterization of Clethodim Metabolites in Plant Tissues						
	ppm (calculated as clethodim from ^{14}C -labeled clethodim)					
Component	Soybean Bean	Soybean Foliage	Cotton seed	Cotton Foliage	Carrot Root	Carrot Leaves
C	---	---	---	---	0.003	---
CSO	1.24	1.65	0.003	0.55	0.11	3.50
CSO_2	0.178	0.25	0.002	0.054	0.014	0.13
ISO	0.302	3.88	0.004	2.40	0.040	4.93
ISO_2	0.314	2.43	0.002	0.55	0.034	1.32
5OH-SO	0.275	<0.05	<0.001	0.19	0.026	0.36
5OH-SO_2	0.414	0.86	0.001	0.054	0.030	0.42
Arom. SO_2	0.58	0.14	<0.001	0.068	0.006	0.067
Others	0.271[a]	3.63[a]	0.0045[b]	4.22[a]	0.052[a]	2.419[a]
CSO-Conj.	0.329	6.92	<0.001	0.37	0.024	1.90
CSO_2-Conj.	0.050	0.56	<0.001	0.18	0.002	0.11
Other Conj.	0.383[a]	5.11[a]	0.020[c]	4.25[a]	0.041[b]	5.98[a]
Non-extractable	0.058	2.48	0.032	0.62	0.015	1.18
Totals	3.872	27.94	0.069	13.51	0.397	22.32

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[a] Composed of ≥9 ^{14}C metabolites
[b] Composed of ≥4 ^{14}C metabolites
[c] Contained radioactivity too low to allow further characterization.
Abbreviations are referenced in the previous text.

HED Comments/Conclusions:

No new plant metabolism study has been submitted with this petition. Metabolism studies for clethodim in/on carrots, soybeans, and cotton were previously reviewed (PP#9F3743, MRIDs 41030137 & 41030138, M. Nelson, 3/12/90). The qualitative nature of the clethodim residue in plants is adequately understood for root crops and oil seed crops. HED previously concluded that the residues of concern are clethodim and its metabolites containing the 2-cyclohexen-1-one moiety. However, the residues of concern are now described as clethodim and metabolites containing the 5-(2-(ethylthiopropyl)cyclohexene-3-one and 5-(2-(ethylthiopropyl)-5-hydroxycyclohexene-3-one moieties and their sulphoxides and sulphones in order to harmonize with the Codex MRL (PP#4F4340, D203378, J. Morales, 1/31/95).

For future petitions on crops other than root crops and oil seed crops, additional metabolism data may be required.

OPPTS GLN 860.1300: Nature of the Residue - Livestock

A metabolism study has been previously submitted and reviewed: "The in vivo Metabolism of [propyl-1-^{14}C]-Clethodim in a Lactating Goat," 12/29/88, Lab ID# MEF-0038, MRID# 410301-39 (PP#9F3743, M. Nelson, 3-12-90).

The total radioactive residue in milk plateaued at about 0.035 ppm by the evening of day two. The milk was lyophilized for solvent extraction of metabolites. About half the ^{14}C activity was extractable into organic solvents. It was composed of clethodim (≤0.001 ppm), clethodim sulfoxide (0.006-0.013 ppm), and S-methyl sulfoxide (0.001-0.005 ppm). The other half of the ^{14}C activity was water-soluble and was shown by isotopic dilution to be ^{14}C-lactose (0.014-0.017 ppm, as clethodim equivalents).

Most (77-95%) of the ^{14}C activity in tissues and blood was extractable into organic solvents, with the acetonitrile and methanol-water fractions containing the highest levels of activity. Those two fractions were pooled for residue characterization, and the metabolic profiles of that extractable activity are given in Table 2.

The dominant metabolic process in the ruminant (goat) is oxidation of clethodim to clethodim sulfoxide and, to a lesser extent, clethodim sulfone. Clethodim can also be converted to the S-methyl derivative, which can be oxidized to S-methyl sulfoxide and S-methyl sulfone derivatives. Cleavage of the oxime N-O bond in clethodim produces the imine, which is rapidly

oxidized to imine sulfoxide. In a minor process, clethodim can be hydroxylated to 5-OH, which can be oxidized to 5-OH sulfoxide. Alternately, clethodim sulfoxide may be hydroxylated to 5-OH sulfoxide. The S-methyl derivative is formed only from clethodim; the literature does not support the formation of S-methyl sulfoxide from clethodim sulfoxide. Thus, the S-methyl metabolites have significance only if animals are exposed to clethodim, and this is limited because clethodim is rapidly oxidized to sulfoxides and sulfones in plants.

Table 2. Clethodim metabolite profile (ppm) in goat tissue and blood[a]

Component	Blood	Liver	Kidney	Heart	Muscle Fqtr.	Muscle Hqtr.	Subcut. Fat
C	0.047	0.114	0.005	0.000	0.000	0.000	0.002
CSO	0.067	0.137	0.139	0.025	0.017	0.014	0.037
CSO_2	0.006	0.013	0.000	0.000	0.000	0.000	0.000
SMSO	0.019	0.025	0.116	0.021	0.009	0.011	0.023
ISO	0.005	0.006	0.016	0.000	0.000	0.000	0.004
5OH-SO_2	0.004	0.000	0.000	0.000	0.000	0.000	0.000
Unknown[b]	0.005	0.016	0.037	0.000	0.000	0.003	0.006

[a] Values reported as 0.000 ppm are below the level of claimed sensitivity, which is <0.001

[b] The unidentified activity was polar in nature and remained at the origin (TLC).

HED Comments/Conclusions:

Metabolism studies of [propyl-1-^{14}C]-clethodim in a lactating goat and laying hens were reviewed (PP#9F3743, MRID# 41030139 & 41030140, M. Nelson, 3/12/90). The nature of the residue in ruminants and poultry is adequately understood for the purposes of the subject petition. HED prevously concluded that the residues of concern are clethodim and its metabolites containing the 2-cyclohexen-1-one moiety.

OPPTS GLN 860.1340: Residue Analytical Method - Plants

In conjunction with the magnitude of the residue studies, the petitioner submitted a method description and validation data for Chevron Chemical Method RM-26B (Revision 2 and 3) used to determine residues of clethodim and its metabolites in/on crop commodities.

Method RM-26B-2

Method RM-26B-2 was used for the analyses of residues of clethodim in radish, carrots cucumbers, cranberries and strawberries. The method involves extraction with aqueous methanol, cleanup by alkaline precipitation and acidic back extraction, oxidation to the pentanedioic acid

moieties, derivatization to the corresponding dimethyl esters (DME and/or DME-OH), partition of the dimethyl esters in CH_2Cl_2, and determination by gas chromatography-flame photometric detection in the sulfur mode (GC-FPD-S). The total residue is expressed as clethodim equivalents. This method RM-26B-2 has successfully completed a Petition Method Validation (PMV) in EPA Laboratories (M. Nelson's memo of 5/4/90).

The validated LOQ for residues of DME and DME-OH (calculated as clethodim) are as follows: 0.05 ppm in/on strawberry and cranberry, 0.14 or 0.11 ppm in/on carrots, and 0.16 or 0.29 ppm in/on radish roots.

Method RM-26B-3

Method RM-26B-3 (a modification of RM-26B-2) was used for the analyses of residues of clethodim in/on celery, cantaloupes, and clover. The analyses were conducted in Valent Technical Center, Dublin, CA. Method RM-26B-3 measures total residues of clethodim and its metabolites as two common moieties in plant or animal tissues by gas chromatography. The method cannot distinguish between clethodim and sethoxydim. The method involves extraction with methanol or water, followed by cleanup with alkaline precipitation and acid back extraction into dichloromethane. An alkaline hydrogen peroxide oxidation converts sulfides and sulfoxides to sulfones and then to dicarboxylic acids. The dicarboxylic acids are derivatized to dimethyl esters which are partitioned into dichloromethane; the measurement of the pentanedioic acid dimethyl esters (DME sulfone and DME-OH sulfone) is by gas chromatography-flame photometric detection in the sulfur mode (GC-FPD-S). Quantitation is from a standard curve using DME and DME-OH and the total residue is expressed as clethodim equivalents. For recovery studies, the samples may be fortified with clethodim, clethodim sulfoxide, or 5-OH clethodim sulfone, common metabolites of clethodim in plants. Calculations were provided to show the method of conversion of detected DME or DME-OH to clethodim, clethodim sulfoxide, or 5-OH clethodim sulfone. This method modifies RM-26B-2 by updating measurement parameters and calculation procedures and modifying the silica gel cleanup procedure.

The validated LOQ for residues of DME and DME-OH (calculated as clethodim) are as follows: 0.2 ppm each in/on celery, 0.1 ppm each in/on cantaloupe; 0.5 ppm each in/on clover forage.

Method validation data are presented in Table 3. For method validation, control samples of radish (roots and tops), carrots, cranberry, and strawberry were fortified with clethodim or clethodim sulfoxide and 5-OH-clethodim sulfoxide at 0.05-20.0 ppm. Method recoveries of DME and 5-OH-DME were typically within the acceptable range (70-120%), except for carrots fortified with 5-OH-clethodim sulfoxide at 0.09 ppm, for which recoveries of 5-OH-DME were consistently high ($\bar{x}$=135±13%, n=7). Concurrent recoveries of DME and 5-OH-DME were generally acceptable with some minor exceptions, such as consistently high recoveries of 5-OH-DME ($\bar{x}$=130±17%, n=16) from carrot roots fortified with 5-OH-clethodim sulfoxide at 0.09 ppm, and low recoveries from strawberry of both DME and 5-OH-DME ($\bar{x}$=61-69) at the 2.0 and 20 ppm fortification levels. Apparent residues were nondetectable in/on all control samples.

Table 3. Recovery of clethodim residues from fortified crop control samples analyzed using a GC/FPD method (Chevron Method No. RM-2B-2 or RM-2B-3).

MRID	Matrix	Fortification level (ppm)	Number of samples /analyte	% Recovery			
				DME[a]		5-OH-DME[a]	
				Range	Ave. ± SD	Range	Ave. ± SD
Method Validation Recoveries							
45027803	Radish roots	0.14/0.25[b]	5	88-127 (2)[c]	106 ± 18	62-83 (3)	71 ± 7
	Radish tops	0.14/0.25	4	104-132 (2)	120 ± 14	64-82 (1)	76 ± 8
		1.2/1.1	3	103-107	105 ± 2	76-81	78 ± 3
44753203	Cucumbers	0.11	4	95-117	105 ± 9	87-94	91 ± 3
45027802	Carrot root	0.12/0.09	7	111-122 (1)	117 ± 4	113-151 (6)	135 ± 13
45027807	Cranberry	0.05	3	96-110	101 ± 8	116-124 (2)	121 ± 5
		0.5	4	67-83 (1)	76 ± 7	84-114	98 ± 13
		1.0	5	66-81 (2)	74 ± 6	72-106	92 ± 14
45027808	Strawberry	0.05-20.0	9	44-96 (2)	78 ± 16	43-92 (2)	72 ± 14
Concurrent Method Recoveries							
45027803	Radish root	0.14/0.25	10	86-124 (1)	108 ± 12	66-77 (4)	72 ± 4
	Radish tops	0.14/0.26	8	104-129 (4)	114 ± 13	69-102 (1)	86 ± 11
		1.16/1.06	2	91, 100		80, 94	
45027802	Carrot root	0.09/0.12	16	88-136 (8)	118 ± 15	102-150 (12)	130 ± 17
		1.8/2.3	2	74, 77	76	75, 72	74
45027804	Celery	0.20-5.0	11	77-98	91 ± 6	62-107 (1)	88 ± 11
45027806	Squash	0.2-2.0	12	64-100 (2)	81 ± 12	62-105 (3)	77 ± 6
44753203	Cucumbers	0.09-1.2	14	86-118	101 ± 12	89-116	105 ± 6
45027805	Cantaloupe	0.1-5.0	18	68-110 (1)	89 ± 12	65-122 (3)	88 ± 15
45027809	Clover forage	0.5-20	8	63-112 (1)	89 ± 17	56-123 (3)	95 ± 9
	Clover hay	0.2-20	7	84-105	81 ± 21	62-88 (2)	75 ± 10
45027807	Cranberry	0.05	2	112, 118	115	146, 156	151
		0.5	1	70	NA	97	NA
		1.0	4	66-89 (1)	74 ± 10	72-108	89 ± 17
45027808	Strawberry	0.05	18	72-114	95 ± 10	54-146 (5)	98 ± 24
		0.5	2	73, 74	73	63, 103 (1)	83
		1.0	1	61	NA	84	NA
		2.0	16	44-86 (10)	65 ± 11	43-92 (9)	69 ± 12
		20.0	6	36-86 (2)	69 ± 18	33-78 (3)	61 ± 17

[a] Samples were fortified with clethodim or clethodim sulfoxide and 5-OH-clethodim sulfoxide.

[b] Indicates that samples were fortified simultaneously with clethodim or clethodim sulfoxide and 5-OH-clethodim sulfoxide, respectively, but at slightly different fortification levels.

[c] Values in parentheses indicate the number of samples with recoveries outside the 70-120% acceptable range.

HED Comments/Conclusions:

Method RM-26B-2 was validated for the analyses of residues of clethodim and its metabolites in/on radish, carrots cucumbers, cranberries, and strawberries. The fortification levels were 0.14 ppm and 0.25 ppm for radish, 0.09 ppm - 0.23 ppm for carrots, 0.09 ppm - 1.2 ppm for cucumbers, 0.05 ppm - 1.0 ppm for cranberries, and 0.05 ppm - 20 ppm for strawberries. Average recoveries for all commodities were within the acceptable range at all fortification levels tested. The method RM-26B-2 for the determination of clethodim and its metabolites in radish, carrots, cucumbers, cranberries and strawberries is acceptable for data collection and enforcement purposes.

Method RM-26B-3 (a modification of RM-26B-2) was validated for the analyses of residues of clethodim and its metabolites in/on celery, cantaloupes, and clover. The fortification levels were 0.5 ppm and 5.0 ppm for celery, 0.1 ppm - 5.0 ppm for cantaloupes, 0.5 ppm - 2.0 ppm for clover forage, and 0.2 ppm - 20 ppm for clover hay. Average recoveries for all commodities were within the acceptable range at all fortification levels tested. The method RM-26B-3 for the determination of clethodim and its metabolites in celery, cantaloupes, and clover is acceptable for data collection.

The common moiety method RM-26B-3 for the determination of clethodim and its metabolites is similar to the common moiety method RM-26B-2. The method RM-26B-2 has previously undergone a successful Petition Method Validation by the Agency (PP#9F3734, MRID 41389901, M. Nelson, 5/4/90), and a confirmatory method, RM-26D-2 is also available. Both methods (RM-26B-2 & RM-26D-2) have been forwarded to FDA as enforcement methods for inclusion in PAM II.

OPPTS GLN 860.1340: Analytical Methods - Animals

The Agency has previously concluded (DP Barcode D194694, F. Griffith, 9/29/93) that adequate analytical methodology is available to enforce tolerances for residues of clethodim in animal commodities. The compound specific method, EPA-RM-26D-2, is suitable for enforcement of tolerances for total clethodim residues in crops and animal tissues, and it has been forwarded to FDA for publication in the Pesticide Analytical Manual, Volume II (PAM II). The common moiety method, RM-26B-2, serves as the enforcement method for milk as RM-26D-2 is not quantitative for milk.

OPPTS GLN 860.1360: Multiresidue Method

The petitioner has previously submitted data (1991; MRID 43166406, and 1992; MRID 43166407) describing the testing of clethodim through FDA Multiresidue Methods. These data, which have been forwarded to FDA for review, indicate that adequate recoveries of clethodim, clethodim sulfoxide, and 5-OH clethodim sulfone have been obtained under FDA's multiresidue protocols (PP#9F3743, M. Nelson's memo of 3/12/90).

OPPTS GLN 860.1380: Storage Stability Data

In conjunction with the magnitude of the residue studies, untreated samples of carrots, radish, celery, cucumbers, summer squash, cantaloupe, clover, cranberries, and strawberries were fortified with both clethodim (or more typically clethodim sulfoxide) and 5-OH-clethodim shortly after collection and were placed in frozen storage. The stored fortified samples were then analyzed at intervals corresponding to storage intervals incurred by samples from the respective crop field trials. Table 4 summarizes the parameters and recovery results for the current stability tests on each of the commodities associated with the subject petition.

Table 4. Storage stability of clethodim residues in crop commodities

Crop/MRID	Analytes fortified	Storage interval (days)	Spike level (ppm)	Recovery as DME or 5-OH-DME		Max field sample storage interval (days)
				Fresh fortification	Stored Sample	
Carrot 45027802	clethodim sulfoxide	713-720	1.8	77, 74	69, 73, 76, 77	659
	5-OH-clethodim sulfone		1.6	75, 72	64, 66, 69, 73	
Radish (roots) 45027803	clethodim sulfoxide	475	1.1	120	78, 76	552
	5-OH-clethodim sulfone		1.0	75	62, 58	
Radish (tops) 45027803	clethodim sulfoxide	625-636	1.1	91, 100	67, 73, 85, 88	744
	5-OH-clethodim sulfone		1.0	83, 94	69, 73, 78, 84	
Celery 45027804	clethodim + clethodim imine sulfone *	739	2.0	77, 88	70, 75	704
	5-OH-clethodim			62, 88	55, 56	
Cucumber 44753203	clethodim sulfoxide	518-526	1.1	89, 104	91, 75, 89, 93	458
	5-OH-clethodim sulfone		1.0	102, 111	101, 89, 96, 98	
Summer Squash 45027806	clethodim sulfoxide	449-484	2.0	98, 100, 86	88, 94, 81, 99	349
	5-OH-clethodim sulfone			90, 105, 77	80, 88, 80, 85	
Cantaloupe 45027805	clethodim	676-689	0.1	83-109	76, 78, 79	717
			2.0		52, 71, 65	
	clethodim sulfoxide	474	2.0	110	106, 90	
		564		78	71, 81	
	5-OH-clethodim sulfone	474	2.0	122	106, 95	
		564		69, 86	67, 73	
		676-689	0.1	76-99	83, 83, 90	
			2.0		61, 74, 66	
Clover (forage) 45027809	clethodim sulfoxide	309	2.0	63	80, 70	257
	5-OH-clethodim sulfone			56	71, 59	

(Continued; footnotes follow)

Crop/MRID	Analytes fortified	Storage interval (days)	Spike level (ppm)	Recovery as DME or 5-OH-DME		Max field sample storage interval (days)
				Fresh fortification	Stored Sample	
Clover (hay) 45027809	clethodim sulfoxide	297		104	84, 93	
	5-OH-clethodim sulfone			83	77, 86	
Cranberry 45027807	clethodim sulfoxide and	673	2.0	118, 89	76, 64, 64	731
	5-OH-clethodim sulfone			156, 108	88, 75, 78	
Strawberry 45027808	clethodim + clethodim imine sulfone [a]	805-810	2.0	70, 77	71, 60, 81	842
	5-OH-clethodim			81, 92	71, 64, 91	

[a] These analytes are both detected as DME by the method. The recovery is for the combined residues of both analytes (celery) or of clethodim alone (strawberry) corrected for the addition of the imine sulfone by dividing the result by 2.

HED Comments/Conclusions:

The submitted storage stability data are adequate to support the residue field trials for carrots, radish, celery, cucumbers, summer squash, cantaloupe, clover, cranberries and strawberries. The storage stability data showed that residues of clethodim and its metabolites are stable under frozen storage for 720 days (24 months) in carrots, 475 days (16 months) in radish, 739 days (24.6 months) in celery, 526 days (17.5 months) in cucumbers, 484 days (16 months) in summer squash, 689 days (23 months) in cantaloupes, 309 days (10 months) in clover forage, 297 days (10 months) in clover hay, 673 days (22.4 months) in cranberries, and 810 days (27 months) in strawberries. Correction of the residue data for storage degradation is not required.

OPPTS GLN 860.1500: Magnitude of the Residue - Plants

Root Vegetables (except sugar beets) crop subgroup 1b

The petitioner submitted data (citations shown below) from eight carrot field trials conducted during 1994 and 1995 in CA(4), FL (1), MI (1), TX (1), and WA (1), and four radish residue trials conducted in 1993 in FL (1), MI (1), NY (1), and WA (1) to support the proposed tolerance for residues of clethodim and its metabolites in/on root vegetables (except sugar beets) crop subgroup.

45027802 Lai, J.C., Kunkel, D.L., Corley, J. (1999) IR-4 Minor Use Submission in Support of the Proposed Tolerance for Clethodim on Carrot: Laboratory Identification Number 05217.94-MIR15. Unpublished study prepared by the Interregional Research Project Number 4. p. 342

45027803 Corley, J. (1999) IR-4 Minor Use Submission in Support of the Proposed

Tolerance for Clethodim® in/on Radish Roots and Tops. Laboratory Identification Number: 05227.93-MI06. Unpublished study prepared by the Interregional Research Project Number 4. p. 310

Carrots (MRID 45027802). Clethodim (0.94 lb/gal EC) was applied twice foliarly to carrots at 0.236-0.256 lb ai/A/application, at 14-15 day RTIs, for a total seasonal rate of 0.480-0.512 lb ai/A (~1x the maximum proposed rate). Applications were made with ground equipment using 19-86 gallons of water/A; crop oil concentrate was added at 1% v/v to the final spray mixture.

Duplicate control and treated samples of carrots were harvested 29-31 days post-treatment. The tops were removed and the root samples were stored frozen within 2.5 hours of collection. Samples were later shipped frozen by overnight courier (on dry ice) or ACDS freezer truck to the Pesticide Research Center, Michigan State University, East Lansing, MI, where the samples were held at -20±5 C prior to analysis; samples from the trial conducted in MI were hand delivered fresh to the analytical laboratory within 1 hour of collection and frozen immediately. The maximum frozen storage intervals for carrot root samples, from collection to analysis, were 222-659 days (7-22 months).

Residues of clethodim and its metabolites were determined using the adequate GC/FPD method (Method No. RM-2B-2) described above. Concurrent recoveries of clethodim sulfoxide (88-136%; $\bar{x}$ =118±15%, n=16) and 5-OH-clethodim sulfone (102-150%; $\bar{x}$ = 130±17%, n=16) from carrots were high at fortification levels (0.1159 and 0.0925 ppm, as DME and DME-OH, respectively) corresponding to the residue levels observed in the field trial samples. Apparent residues of DME and 5-OH-DME (as parent) were each <LOQ (<0.14 or <0.11 ppm, respectively) in/on 16 control carrot samples. The results of the carrot residue field trials are depicted in Table 5.

Radish (MRID 45027803). Clethodim (0.94 lb/gal EC) was applied once foliarly to radish at 0.246-0.252 lb ai/A/season (1x the maximum proposed rate). Applications were made with ground equipment using 20-35 gallons of water/A; crop oil concentrate was added at 1% v/v to the final spray mixture.

Quadruplicate control and treated samples of radishes, later composited to produce 2 or 3 separate samples from each test for analysis, were harvested 14 or 15 days post-treatment and separated into tops and roots and were placed in frozen storage within 1.5 hours of collection; samples from the MI test site were hand delivered (on ice) and samples from other locations were shipped frozen by ACDS freezer truck to the Pesticide Research Center, Michigan State University, East Lansing, MI, where the samples were held at -20 C prior to analysis. The maximum frozen storage intervals for radish samples, from collection to analysis, were 552 days for roots (18 months) and 744 days for tops (25 months).

Residues of clethodim and its metabolites were determined using the GC/FPD method (Method No. RM-2B-2) described above. Acceptable concurrent recoveries of clethodim sulfoxide and 5-

OH-clethodim sulfone were generally obtained from roots and tops, although several recoveries of clethodim sulfoxide fortified in tops at 0.14 ppm (as DME) were high (123-129%). Apparent residues of DME and 5-OH-DME (as parent) were each <LOQ (<0.16 or <0.29 ppm, respectively) in/on each of eight control radish root and top samples. The results of the residue field trials on radish roots and tops are depicted in Tables 5 and 6.

Table 5. Combined residues of clethodim and its metabolites in/on carrots harvested after two foliar application of clethodim (0.94 lb/gal EC) totaling 0.5 lb ai/A/season (1x the maximum proposed rate) and in/on radishes after a single application of clethodim at 0.25 lb ai/A/season (1x the maximum proposed rate).

Location	EPA Region	Rate (lb ai/A)	PTI [b]	Clethodim Residues (ppm) [a]		
				DME [c]	DME-OH [c]	Combined
Carrots						
CA91	10	0.246 + 0.244 (0.490) [d]	29	<0.14	ND [e]	<0.25
				<0.14	<0.11	<0.25
CA92	10	0.236 + 0.244 (0.480)	31	<0.14	<0.11	<0.25
				<0.14	ND	<0.25
FL	3	0.25 + 0.25 (0.50)	30	<0.14	ND	<0.25
				<0.14	<0.11	<0.25
TX	6	0.256 + 0.256 (0.512)	29	0.18	<0.11	<0.29
				0.28	<0.11	<0.39
CA48	10	0.243 + 0.238 (0.481)	29	0.25	<0.11	<0.36
				0.22	<0.11	<0.33
CA49	10	0.255 + 0.254 (0.509)	31	<0.14	<0.11	<0.25
				<0.14	<0.11	<0.25
MI	5	0.245 + 0.236 (0.481)	31	<0.14	<0.11	<0.25
				<0.14	ND	<0.25
WA	11	0.252 + 0.244 (0.496)	31	<0.14	<0.11	<0.25
				<0.14	<0.11	<0.25
Radish Roots						
MI	5	0.252	15	<0.16	<0.29	<0.45
				<0.16	<0.29	<0.45
WA	11	0.249	14	<0.16	<0.29	<0.45
				<0.16	<0.29	<0.45
				<0.16	<0.29	<0.45
NY	1	0.252	14	<0.16	<0.29	<0.45
				<0.16	<0.29	<0.45
FL	3	0.246	15	<0.16	<0.29	<0.45
				<0.16	<0.29	<0.45

[a] Expressed as parent clethodim.
[b] PTI = Post-treatment Interval (days)
[c] Acronyms for the dimethyl esters of 3-[2-(ethylsulfonyl) propyl]pentanedioic acid and 3-[2-

(ethylsulfonyl)propyl]-3-hydroxypentanedioic acid, respectively.

[d] Total rate is listed parenthetically.

[e] ND = Nondetectable.

HED Comments/Conclusions:

The submitted carrot and radish field trial data and geographic representation for the root vegetables (except sugar beets) crop subgroup 1b are adequate to satisfy the requirements described in OPPTS 860.1500 for a tolerance. Eight carrot field trials were conducted in CA (4), FL (1), MI (1), TX (1), and WA (1); and four radish trials were conducted in FL (1), MI (1), NY (1) and WA (1). Carrot samples were harvested 29-31 days following the last of two applications of clethodim (0.94 lb/gal EC) at 0.236-0.256 lb ai/A/application, at 14-15 day retreatment intervals (RTI), for a total of 0.480-0.512 lb ai/A/season (~1x the maximum proposed rate). Combined residues of clethodim and its metabolites ranged from <0.25 to <0.39 ppm. Radish root samples were harvested 14-15 days post-treatment following a single treatment with clethodim at 0.246-0.252 lb ai/A/season (1x rate). Combined residues were <0.45 ppm (<LOQ) in/on all radish samples. The submitted residue data indicate that the proposed 1.0 ppm tolerance for residues of clethodim and its metabolites in/on the root vegetables except sugar beets (crop subgroup 1b) is adequate.

Leaves of Root and Tuber Vegetables (excluding sugar beets) crop group 2

In conjunction with the residue field trials on radish roots and tops discussed above (MRID 45027803), the petitioner proposes a tolerance of 0.5 ppm for residues of clethodim and its metabolites in/on the leaves of root and tuber vegetables crop group (2), excluding sugar beets. Four radish field trials were conducted in 1993 in FL (1), MI (1), NY (1), and WA (1) following a single treatment with clethodim (0.94 lb/gal EC) at 0.25 lb ai/A/season (1x rate). Combined residues of clethodim and its metabolites for radish top are shown in Table 6.

Table 6. Combined residues of clethodim and its metabolites in/on radish tops after a single application of clethodim at 0.25 lb ai/A/season (1x the maximum proposed rate)

Location	EPA Region	Rate (lb ai/A)	PTI [b]	Clethodim Residues (ppm) [a]		
				DME [c]	DME-OH [c]	Combined
MI	5	0.252	15	0.29	<0.29	<0.58
				0.27	<0.29	<0.56
WA	11	0.249	14	0.28	<0.29	<0.57
				0.25	<0.29	<0.54
NY	1	0.252	14	0.17	<0.29	<0.46
				0.20	<0.29	<0.49
FL	3	0.246	15	0.23	<0.29	<0.52
				0.22	<0.29	<0.51

[a] Expressed as parent clethodim.

[b] PTI = Post-treatment Interval (days)

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- Acronyms for the dimethyl esters of 3-[2-(ethylsulfonyl) propyl]pentanedioic acid and 3-[2-(ethylsulfonyl)propyl]-3-hydroxypentanedioic acid, respectively

HED Comments/Conclusions:

The submitted radish top residue data and geographic representation for the leaves of root and tuber vegetables (excluding sugar beets) crop group 2 are adequate to satisfy the requirements described in OPPTS 860.1500 for a tolerance. Four radish top trials were conducted in FL (1), MI (1), NY (1) and WA (1) following a single treatment with clethodim (0.94 lb/gal EC) at 0.25 lb ai/A/season (1x rate), and harvested 14-15 days post-treatment. Combined residues of clethodim and its metabolites were <0.46-<0.58 ppm in/on eight samples of radish tops. These data indicate that the proposed 2.0 ppm tolerance for residues of clethodim in/on the leaves of root and tuber vegetables (excluding sugar beets) crop group 2 is too high; the appropriate tolerance for residues of clethodin in/on the leaves of root and tuber vegetables (excluding sugar beets) crop group 2 should be 1.0 ppm. Therefore, a revised Section F must be submitted proposing a tolerance at 1.0 ppm for residues of clethodim and its metabolites in/on the leaves of root and tuber vegetables.

Leaf Petioles Crop Subgroup 4a

The petitioner submitted data (citation shown below) from five celery field trials conducted during 1994 and 1995 in CA(2), FL (1), MI (1), and TX (1).

> 45027804 Braverman, M.P. (1999) Clethodim: Magnitude of the Residue on Celery: Laboratory Identification Number 05218.96-VAL02. Unpublished study prepared by the Interregional Research Project-4. p 161.

Clethodim (0.94 lb/gal EC) was applied twice foliarly to celery at 0.24-0.29 lb ai/A/application, at 14- or 15-day RTIs, for a total seasonal rate of 0.49-0.57 lb ai/A (~1x the maximum proposed rate). Applications were made with ground equipment using 19-93 gallons of water/A with crop oil concentrate added at 1% v/v (0.4% v/v in TX) to the final spray mix.

Duplicate control and treated samples of celery were collected 29-31 days post-treatment. Samples from the test conducted in TX during 1995 were stored frozen within 2 hours of collection and later shipped by overnight courier (on dry ice) directly to the analytical laboratory, Valent Technical Center, Dublin, CA. Samples from all other studies (1994 trials) were placed in frozen storage within 2 hours of harvest, and were later shipped frozen by ACDS freezer truck to the Yakima Agricultural Research Laboratory, Yakima, WA. At Yakima, the samples were held frozen (- 15 C) prior to reshipment by ACDS to the Pesticide Research Laboratory of Penn State University, University Park, PA, where the samples were prepared for analysis by maceration and stored at -18 C. The samples were then shipped frozen via ACDS to Valent Technical Center and stored at ≤-15 C prior to analysis. The maximum sample frozen storage interval from harvest to analysis was 704 days (23 months).

Residues of clethodim and its metabolites were determined using the adequate GC/FPD method (Method No. RM-2B-3) described above. Acceptable concurrent recoveries of clethodim ($\bar{x}$ = 91±6%) and 5-OH-clethodim sulfone ($\bar{x}$ = 88±11%) were obtained from celery fortified with each analyte at 0.2-5.0 ppm. Apparent residues of DME and 5-OH-DME were each nondetectable (<0.10 ppm) in/on ten control celery samples. The results of the celery residue field trials are depicted in Table 7.

Table 7. **Combined residues of clethodim and its metabolites in/on celery harvested after two foliar applications of clethodim (0.94 lb/gal EC), at 14- or 15-day RTIs, totaling ~0.5 lb ai/A (1x the proposed maximum rate)**

Location	EPA Region	Rate (lb ai/A)	PTI [a] (days)	Clethodim Residues (ppm) [b]		
				DME [c]	DME-OH [c]	Combined
CA1	10	0.249 + 0.240 (0.489) [d]	29	0.33 0.33	<0.20 <0.20	<0.53 <0.53
CA2	10	0.249 + 0.245 (0.494)	31	<0.20 <0.20	<0.20 <0.20	<0.22 <0.24
MI	5	0.243 + 0.248 (0.491)	31	<0.20 <0.20	<0.20 <0.20	<0.20 <0.20
FL	3	0.28 + 0.29 (0.57)	31	<0.20 <0.20	<0.20 <0.20	<0.24 <0.24
TX	6	0.254 + 0.255 (0.509)	30	0.26 0.31	<0.20 <0.20	<0.36 <0.41

[a] PTI = Post-treatment Interval (days).

[b] Expressed as clethodim.

[c] Acronyms for the dimethyl esters of 3-[2-(ethylsulfonyl) propyl]pentanedioic acid and 3-[2-(ethylsulfonyl)propyl]-3-hydroxypentanedioic acid, respectively.

[d] Total rate depicted in parentheses.

HED Comments/Conclusions:

The submitted celery residue data and geographic representation for the leaf petioles crop subgroup 4b are adequate to satisfy the requirements described in OPPTS 860.1500 for a tolerance. Five celery field trials were conducted in CA (2), FL (1), MI (1), and TX (1). Samples were harvested 29-31 days following the last of two applications at 0.24-0.29 lb ai/A/application, at 14- or 15-day RTIs, for a total seasonal rate of 0.49-0.57 lb ai/A (~1x the maximum proposed rate). Combined residues of clethodim were <0.40 - <0.53 ppm in/on celery. The proposed tolerance of 0.5 ppm for residues of clethodim in/on the leafy petioles (crop subgroup 4b) is not adequate; the appropriate tolerance for residues of clethodim and its metabolites in/on the leafy petioles (crop subgroup 4b) should be 1.0 ppm. Therefore, a revised Section F must be submitted proposing a tolerance at 1.0 ppm for the leafy petioles crop subgroup 4b.

Melons Crop Subgroup 9a

The petitioner submitted data (citation shown below) from eight cantaloupe residue field trials conducted during 1994-1997 in CA (3), FL (1), MI (1), SC (2), and TX (1).

> 45027805 Corley, J. (1999) Clethodim: Magnitude of the Residue on Cantaloupe: Laboratory Identification Number 05225.96-VAL03. Unpublished study prepared by the Interregional Research Project Number 4. p. 261

Clethodim (0.94 lb/gal EC) was applied twice foliarly to cantaloupe at 0.243-0.316 lb ai/A/application, at 12-14 day RTIs, for a total seasonal rate of 0.490-0.619 lb ai/A (~1x the maximum proposed rate). Applications were made with ground equipment using 19-42 gallons of water/A; crop oil concentrate or non-ionic surfactant were added at 1% v/v to the final spray mixture.

Duplicate control and treated samples of cantaloupe were harvested 13-14 days post-treatment (20 days for Trial SC13) and stored frozen within 4.5 hours of collection. Samples from three trials (TX, CA62, SC02) were later shipped frozen by overnight courier (on dry ice) or ACDS freezer truck directly to the analytical laboratory, Valent Technical Center, Dublin, CA, where the samples were held at ≤-7 C prior to analysis. Samples from the remaining trials were shipped frozen by ACDS and temporarily stored at the Department of Food Sciences, Cornell-NYSAES, Geneva, NY and/or the Pesticide Research Laboratory of Penn State University, University Park, PA (≤-18 C) prior to reshipment to Valent Technical Center for analysis. The samples were maintained at ≤-7 C, from collection to analysis, for a maximum of 717 days (24 months).

Residues of clethodim and its metabolites were determined using the adequate GC/FPD method (Method No. RM-26B-3) described above. Acceptable concurrent recoveries of clethodim or clethodim sulfoxide ($\bar{x}$ =89±12%) and 5-OH-clethodim sulfone ($\bar{x}$ = 88±15%) were obtained from cantaloupe fortified with each analyte at 0.1-5.0 ppm. Apparent residues of DME and 5-OH-DME were each <0.10 ppm (<LOQ) in/on ten control cantaloupe samples. The results of the cantaloupe residue field trials are depicted in Table 8.

Table 8. Combined residues of clethodim and its metabolites in/on cantaloupe harvested after two foliar applications of clethodim (0.94 lb/gal EC) totaling 0.5 lb ai/A/season (1x the proposed maximum rate)

Location	EPA Region	Rate (lb ai/A)	PTI [b]	Clethodim Residues (ppm) [a]		
				DME [c]	DME-OH [c]	Combined
TX	6	0.251+0.256 (0.507) [d]	13	<0.10 [e]	<0.10	<0.20
				<0.10	<0.10	<0.20
MI	5	0.243 + 0.260 (0.503)	14	0.95, 1.1, 1.1	<0.10, <0.10, <0.10	<1.05, <1.2, <1.2
				1.1, 1.2	<0.10, <0.10	<1.2, <1.3
FL	3	0.247 +0.244 (0.491)	14	0.16	<0.10	<0.26
				0.16	<0.10	<0.26
SC13	2	0.316 + 0.303 (0.619)	20	<0.10, <0.10	<0.10, <0.10	<0.20, <0.20
				<0.10, 0.11	<0.10, <0.10	<0.20, <0.21
CA51	10	0.245 + 0.245 (0.490)	14	0.16	<0.10	<0.26
				0.12	<0.10	<0.22
CA52	10	0.245 + 0.245 (0.490)	14	0.28	<0.10	<0.38
				0.30	<0.10	<0.40
SC02	2	0.252 + 0.249 (0.501)	13	0.13	<0.10	<0.23
				0.12	<0.10	<0.22
CA62	10	0.247 + 0.248 (0.495)	13	0.25	<0.10	<0.35
				0.22	<0.10	<0.32

[a] Expressed as parent clethodim; results depict up to triplicate analyses of single samples.
[b] PTI = Post-treatment Interval (days).
[c] Acronyms for the dimethyl esters of 3-[2-(ethylsulfonyl) propyl]pentanedioic acid and 3-[2-(ethylsulfonyl)propyl]-3-hydroxypentanedioic acid, respectively.
[d] Total rate depicted in parentheses.
[e] The validated LOQ for residues in/on cantaloupe is 0.10 ppm.

HED Comments/Conclusions:

The submitted cantaloupe residue data and geographic representation for the melon crop subgroup 9a are adequate to satisfy requirement described in OPPTS 860.1500 for a tolerance. Eight cantaloupe field trials were conducted in CA (3), FL (1), MI (1), SC (2), and TX (1). Samples harvested 13-14 days (20 days, one test) following the last of two applications at 0.243-0.316 lb ai/A/application, at 12-14 day RTIs, for a total of 0.490-0.619 lb ai/A/season (~1x the maximum proposed rate). Combined residues of clethodim and its metabolites were <0.20-<1.3 ppm in/on cantaloupes. These data indicate that the proposed tolerance of 2.0 ppm for residues of clethodim in/on the melon crop subgroup is adequate.

Squash/Cucumber Crop Subgroup 9b

The petitioner submitted data (citations listed below) from five residue field trials conducted on summer squash during 1996-1997 in CA (1), FL (1), MI (1), NY (1), and SC (1), and six trials

conducted on cucumbers in 1994-1995 in FL (1), MI (1), NY (1), SC (1), TX (1), and WI (1).

45027806 Corley, J. (1999) Clethodim: Magnitude of the Residue on Squash (Summer): Laboratory Identification Number 05228.96-VAL05. Unpublished study prepared by the Interregional Research Project Number 4. p. 188

44753203 Lai, J. C., and D. L., Kunkel. (1998) Clethodim: Magnitude of the Residue on Cucumber: Laboratory Identification Number 05219. Unpublished study prepared by the Interregional Research Project Number 4. p. 251.

Summer Squash (MRID 45027806). Clethodim (0.94 lb/gal EC) was applied twice foliarly to summer squash at 0.237-0.256 lb ai/A/application, at 11-15 day RTIs, for a total seasonal rate of 0.478-0.507 lb ai/A (~1x the maximum proposed rate). Applications were made with ground equipment using 19-35 gallons of water/A; crop oil concentrate or non-ionic surfactant were added at 1% v/v to the final spray mixture.

Duplicate control and treated samples of squash were harvested 13-14 days post-treatment and frozen within 1 hour of collection. The samples were later shipped frozen by ACDS freezer truck to the analytical laboratory, Valent Technical Center, Dublin, CA, where the samples were held at ≤-7 C prior to analysis; samples from the trial conducted in NY were delivered (on ice) by the field cooperator to Cornell Analytical Laboratories, Geneva, NY, where they were stored at ≤-18 C prior to frozen reshipment by ACDS to Valent. The samples were stored frozen (≤-7 C), from collection to analysis, for a maximum of 349 days (12 months).

Residues of clethodim and its metabolites were determined using the adequate GC/FPD method (Method No. RM-26B-3) described above. Acceptable concurrent recoveries of clethodim or clethodim sulfoxide ($\bar{x}$ =81±12%) and 5-OH-clethodim sulfone ($\bar{x}$ = 77±12%) were obtained from squash fortified with each analyte at 0.2-2.0 ppm. Apparent residues of DME and 5-OH-DME were each <0.10 ppm (<LOD) in/on ten control squash samples. The results of the crop field trials on summer squash are depicted in Table 9.

Cucumbers (MRID 44753203). Clethodim (0.94 lb/gal EC) was applied twice foliarly to cucumbers at 0.25 lb ai/A/application, at 12-14 day RTIs, for a total seasonal rate of 0.50 lb ai/A (~1x the maximum proposed rate). Applications were made with ground equipment using 19-34 gallons of water/A; crop oil concentrate or non-ionic surfactant were added at 1% v/v to the final spray mixture.

Duplicate control and treated samples of cucumbers were harvested 13-14 days post-treatment and frozen within 80 minutes of collection. Samples from the MI test site were hand delivered and placed in frozen storage within 1 hour and 20 minutes; other samples were shipped frozen by personal vehicle and/or ACDS freezer truck, or overnight courier (on dry ice), to the analytical laboratory, the Pesticide Research Center, Michigan State University, East Lansing, MI, where the samples were held at -20 ±5 C prior to analysis. The samples were stored frozen, from

collection to analysis, for a maximum of 458 days (15 months).

Residues of clethodim and its metabolites were determined using the adequate GC/FPD method (Method No. RM-2B-2) described above. Acceptable concurrent recoveries of clethodim sulfoxide ($\bar{x}$= 101±12%) and 5-OH-clethodim sulfone ($\bar{x}$ = 105±6%) were obtained from cucumbers fortified with each analyte at 0.09-1.2 ppm. Apparent residues of DME and 5-OH-DME were each <LOQ (<0.13 or <0.14 ppm, respectively) in/on all control cucumber samples. The results of the crop field trials on cucumbers are depicted in Table 9.

Table 9. Combined residues of clethodim and its metabolites in/on **summer squash** and **cucumber** harvested after two foliar applications of clethodim (0.94 lb/gal EC) totaling 0.5 lb ai/A/season (1x the proposed maximum rate)

Location	EPA Region	Rate (lb ai/A)	PTI [b]	Clethodim Residues (ppm) [a]		
				DME [c]	DME-OH [c]	Combined
Summer squash						
CA	10	0.256 + 0.248 (0.507) [d]	13	<0.10	<0.10	<0.20
				<0.10	<0.10	<0.20
MI	5	0.237 + 0.241 (0.478)	14	0.11	<0.10	<0.21
				<0.10	<0.10	<0.20
FL	3	0.248 + 0.248 (0.496)	14	<0.10	<0.10	<0.20
				<0.10	<0.10	<0.20
NY	1	0.250 + 0.250 (0.500)	14	<0.10	<0.10	<0.20
				<0.10	<0.10	<0.20
SC	2	0.255 + 0.252 (0.507)	14	<0.10	<0.10	<0.20
				<0.10	<0.10	<0.20
Cucumber						
NY	1	0.25 + 0.25 (0.50)	14	<0.14 [f]	<0.13 [f]	<0.27
				<0.14	<0.13	<0.27
SC	2	0.25 + 0.25 (0.50)	13	<0.14	<0.13	<0.27
				<0.14	<0.13	<0.27
FL	3	0.25 + 0.25 (0.50)	14	<0.14	<0.13	<0.27
				<0.14	<0.13	<0.27
MI	5	0.25 + 0.25 (0.50)	13	<0.14	<0.13	<0.27
				<0.14	<0.13	<0.27
WI	5	0.25 + 0.25 (0.50)	14	<0.14	<0.13	<0.27
				<0.14	<0.13	<0.27
TX	6	0.25 + 0.25 (0.50)	14	<0.14	<0.13	<0.27
				<0.14	<0.13	<0.27

[a] Expressed as parent clethodim.

[b] PTI = Post-treatment Interval (days).

[c] Acronyms for the dimethyl esters of 3-[2-(ethylsulfonyl) propyl]pentanedioic acid and 3-[2-(ethylsulfonyl)propyl]-3-hydroxypentanedioic acid, respectively.

[d] Total rate depicted in parentheses.

e The value reported is greater that the limit of detection (0.10 ppm) but <LOQ (0.20 ppm).
f The respective LOQs for residues of DME and DME-OH in/on cucumbers.

HED Comments/Conclusions:

The submitted squash (summer) and cucumber residue data and geographic representation for the squash/cucumber crop subgroup 9b are adequate to satisfy requirement described in OPPTS 860.1500 for a tolerance. Five summer squash field trials were conducted in NY (1), SC (1), FL (1), MI (1) and CA (1); and six cucumber field trials were conducted in FL (1), MI (1), NY (1), SC (1), TX (1) , and WI (1). Samples of summer squash were harvested 13 or 14 days following the last of two foliar applications of clethodim (0.94 lb/gal EC) at 0.237-0.256 lb ai/A/application, at 11-15 day RTIs, for a total seasonal rate of 0.478-0.507 lb ai/A (~1x the maximum proposed rate). Cucumber samples harvested 13 or 14 days after two foliar applications of clethodim at 0.25 lb ai/A/application, at 12-14 day RTIs, totaling 0.50 lb ai/A (1x). Combined residues of clethodim were non-quantifiable (<LOQ; or <0.40 ppm) in/on all squash samples. Combined residues of clethodim and its metabolites were also non-quantifiable (<LOQ; or <0.27 ppm) in/on all cucumber samples. The submitted summer squash/cucumber residue data are adequate to support the proposed tolerance of 0.5 ppm for residues of clethodim in/on the squash/cucumber crop subgroup 9b.

Clover

The petitioner submitted data (citation shown below) from three clover field trials conducted in OR during 1995.

> 45027809 Corley, J. (1999) IR-4 Minor Use Submission in Support of the Proposed Tolerance for Clethodim® in/on Clover Grown for Seed: Laboratory Identification Number 06218.95-VAL03. Unpublished study prepared by the Interregional Research Project Number 4. p. 188

Clethodim (0.94 lb/gal EC) was applied once foliarly to clover at 0.25 lb ai/A/season (1x the maximum proposed rate). Applications were made with ground equipment using 20-30 gallons of water/A and crop oil concentrate added at 1% v/v to the final spray mix.

Duplicate control and treated samples of clover forage (with the exception of OR31 for which a single control and treated sample were collected) were harvested 15 days post-treatment; hay samples cut simultaneously with the forage samples were allowed to air-dry in the field for 5-7 days prior to collection. The samples were stored at ≤-16 C within 4 hours of collection and were later shipped by ACDS freezer truck to the analytical laboratory, Valent Technical Center, Dublin, CA, where they were stored at ≤-15 C prior to analysis. The maximum sample frozen storage interval from harvest to analysis was 257 days (9 months).

Residues of clethodim and its metabolites in/on clover commodities were determined using the

adequate GC/FPD method (Method No. RM-2B-3) described above. Acceptable concurrent recoveries were obtained from clover forage fortified with clethodim or clethodim sulfoxide ($\bar{x}$= 89±17%) and 5-OH-clethodim sulfone ($\bar{x}$= 95 ± 9%) at 0.5-20 ppm; recoveries were also acceptable for clethodim or clethodim sulfoxide ($\bar{x}$= 81 ± 21%) and 5-OH-clethodim sulfone ($\bar{x}$= 75 ± 10%) from hay fortified at 0.2-20 ppm. Apparent residues of DME and 5-OH-DME were each <0.10 ppm (<LOD) in/on all control samples of forage and hay. The results of the clover residue field trials are depicted in Table 10.

Table 10. Combined residues of clethodim and its metabolites in/on clover harvested after a single foliar application of clethodim (0.94 lb/gal EC) totaling 0.25 lb ai/A/season (1x the proposed maximum rate)

Location	EPA Region	PTI [a]	Clethodim Residues (ppm) [b]		
			DME [c]	DME-OH [c]	Combined
Forage					
OR31	12	15	3.15, 3.21; 3.22, 3.04 [d]	[<0.10] [e]	<3.25, <3.31; <3.32, <3.14
OR29	12		5.7	0.12	5.82
			6.0	0.12	6.12
OR30	11		5.1	0.11	5.21
			4.6	<0.1	<4.70
Hay					
OR31	12	15 [f]	11, 11; 12, 12 [d]	0.20, 0.15; 0.22, 0.15	11.20, 11.15; 12.22, 12.15
OR29	12		15	0.29	15.29
			12	0.26	12.26
OR30	11		11	0.17	11.17
			12	0.18	12.18

[a] PTI = Post-teatment Interval (days).
[b] Expressed as clethodim.
[c] Acronyms for the dimethyl esters of 3-[2-(ethylsulfonyl) propyl]pentanedioic acid and 3-[2-(ethylsulfonyl)propyl]-3-hydroxypentanedioic acid, respectively.
[d] Results of duplicate analyses of duplicate subsamples of the same sample.
[e] Reported as the limit of detection.
[f] Samples were cut 15 days post-teatment and allowed to air-dry in the test plot for 5-7 days prior to sampling.

HED Comments/Conclusions:

The submitted clover residue data and geographic representation are adequate to satisfy the requirements described in OPPTS 860.1500. Three clover field trials were conducted in OR (3). Samples were harvested 15 days following a single application of clethodim (0.94 lb/gal EC) at 0.25 lb ai/A/season (1x the proposed maximum rate). Combined residues and its metabolites were <3.1-6.1 ppm in/on forage samples and 11.2-15.3 ppm in/on hay samples. These data indicate that the proposed tolerances with regional registration (limited to ID, OR, WA) for residues in/on clover forage (10 ppm) and hay (20 ppm) are adequate.

Cranberry

The petitioner submitted data (citation shown below) from three cranberry field trials conducted during 1994 in MA (1), WI (1), and WA (1).

> 45027807 Samoil, K.S. (1999) IR-4 Minor Use Submission in Support of the Proposed Tolerance for Clethodim in/on Cranberry: Laboratory Identification Number 05358.94-YAR11. Unpublished study prepared by the Interregional Research Project Number 4. p. 136

Clethodim (0.94 lb/gal EC) was applied twice foliarly to cranberries at 0.241-0.277 lb ai/A/application, at 14-21 day RTIs, for a total seasonal rate of 0.492-0.516 lb ai/A (1x the maximum proposed rate). Applications were made with ground equipment using 20-50 gallons of water/A and crop oil concentrate added at 1% v/v to the final spray mix.

Duplicate control and treated samples of cranberries were harvested 29-30 days post-treatment by hand using a cranberry rake or scoop, and they were stored at ≤-8 C within 7.5 hours of collection. The samples were later shipped frozen to the analytical laboratory, USDA-ARS Yakima Agricultural Research Laboratory, Yakima, WA, where they were stored at ≤-12 C prior to analysis; samples from one trial (MA) were first shipped on dry ice to Cornell Analytical Laboratory, Geneva, NY and reshipped by ACDS freezer truck to the analytical laboratory in Yakima, WA. The maximum sample frozen storage interval from harvest to analysis was 731 days (24 months).

Residues of clethodim and its metabolites were determined using the adequate GC/FPD method (Method No. RM-2B-2) described above. Acceptable concurrent recoveries (66-118%) were obtained from cranberries fortified with clethodim or clethodim sulfoxide at 0.05-1.0 ppm; recoveries of 5-OH-clethodim sulfone were high at the 0.05 ppm fortification level (146% and 156%) and within the acceptable range (72-108%) at 0.5 and 1.0 ppm. Apparent residues of DME and 5-OH-DME were each <0.05 ppm (<LOQ) in/on six control berry samples. The results of the cranberry residue field trials are depicted in Table 11.

Table 11. Combined residues of clethodim and its metabolites in/on cranberry harvested after two foliar applications of clethodim (0.94 lb/gal EC), at 14-21day RTIs, totaling ~0.5 lb ai/A (1x the proposed maximum rate)

Location	EPA Region	Rate (lb ai/A)	PTI [a]	Clethodim Residues (ppm) [b]		
				DME [c]	DME-OH [c]	Combined
WI	5	0.277 + 0.239 (0.516) [d]	29	0.18 0.17	0.14 0.14	0.32 0.31
				0.16 <0.05 0.15	0.12 <0.05 0.14	0.28 <0.10 0.29
WA	12	0.251 + 0.241 (0.492)	29	0.08 0.09	0.08 0.09	0.16 0.18
				0.06 0.08	0.06 0.06	0.12 0.14
MA	1	0.25 + 0.25 (0.50)	30	0.13 0.16	0.15 0.14	0.28 0.30
				0.13 0.14	0.13 0.15	0.26 0.29

[a] PTI = Post-treatment Interval (days).

[b] Expressed as clethodim. Individual values represent the results of duplicate or triplicate analyses of the two separate samples collected at each trial site.

[c] Acronyms for the dimethyl esters of 3-[2-(ethylsulfonyl) propyl]pentanedioic acid and 3-[2-(ethylsulfonyl)propyl]-3-hydroxypentanedioic acid, respectively.

[d] Total rate depicted in parentheses.

HED Comments/Conclusions:

The submitted cranberry residue data and geographic representation are adequate to satisfy the requirements described in OPPTS 860.1500. Three cranberry field trials were conducted in MA (1), WI (1), and WA (1). Combined residues of clethodim and its metabolites were 0.12-0.32 ppm in/on cranberry samples harvested 29 or 30 days following the last of two applications of clethodim (0.94 lb/gal EC) at 0.241-0.277 lb ai/A/application, at 14-21 day RTIs, for a total of 0.492-0.516 lb ai/A/season (1x the maximum proposed rate). These data support the proposed tolerance of 0.5 ppm for residues of clethodim in/on cranberries.

Strawberry

The petitioner submitted data (citation shown below) from seven strawberry field trials conducted during 1994 and 1995 in CA(2), FL (1), MI (1), NJ (1), NC (1), and WA (1).

> 45027808 Braverman, M.P., Curry, K.K. (1999) IR-4 Minor Use Submission in Support of the Proposed Tolerance for Clethodim® in/on Strawberries: Laboratory Identification Number: 05230.94-YAR04. Unpublished study prepared by IR-4. p. 279.

Clethodim (0.94 lb/gal EC) was applied twice foliarly to strawberries at 0.230-0.268 lb ai/A/application, at 13- or 14-day RTIs, for a total of 0.47-0.52 lb ai/A/season (~1x the maximum proposed rate). Applications were made with ground equipment using 19-61 gallons of water/A and crop oil concentrate added at 1% v/v to the final spray mix.

Duplicate control and treated strawberry samples were harvested at 4 days (3 days for CA1) and 7 days after the last application. Samples were stored frozen (≤-12 C) within 2.75 hours of harvest and were later shipped by ACDS freezer truck, USDA vehicle, or overnight courier to USDA-ARS Yakima Agricultural Research Laboratory, Yakima, WA, where samples were stored at ≤-12 C prior to analysis. Samples were stored frozen from harvest to extraction for analysis for 357-451 days (12-15 months), with the exception of samples from one test (FL) which were stored frozen for 842 days (28 months).

Residues of clethodim and its metabolites were determined using the GC/FPD-Method No. RM-26B-2 described above. Adequate concurrent recoveries of clethodim sulfoxide were obtained at the 0.05-0.50 ppm fortification levels (73-114%), but were generally low at the 1.0-20.0 ppm fortification levels; recoveries of 5-OH clethodim sulfone were also low at the higher (2.0-20.0 ppm) fortification levels. The results of the strawberry field trials are depicted in Table 12.

Table 12. Combined residues of clethodim and its metabolites in/on strawberries harvested following two foliar applications of clethodim (0.94 lb/gal EC), made at 13-14 day RTIs, for a total of ~0.5 lb ai/A (1x the proposed

maximum rate)

Location	EPA Region	Rate (lb ai/A)	PTI [a]	Clethodim Residues (ppm) [b]		
				DME [c]	5-OH-DME [c]	Combined
FL	3	0.24 + 0.26 (0.500) [d]	4	0.41, 0.28, 0.29	0.23, 0.15, 0.23	0.64, 0.42, 0.51
				0.36, 0.36	0.17, 0.17	0.53, 0.53
			7	0.08, 0.18, 0.18	0.06, 0.13, 0.18	0.14, 0.31, 0.36
				0.22, 0.18	0.16, 0.12	0.38, 0.30
WA	11	0.250 + 0.245 (0.495)	4	0.57, 0.40, 0.33	0.61, 0.39, 0.37	1.18, 0.79, 0.70
				0.55, 0.48	0.64, 0.49	1.19, 0.96
			7	0.37, 0.37	0.52, 0.39	0.89, 0.77
				0.38, 0.31	0.50, 0.36	0.88, 0.66
CA1	10	0.236 + 0.238 (0.474)	3	0.62, 0.58	0.17, 0.18	0.79, 0.76
				0.65, 0.60	0.14, 0.18	0.79, 0.77
			7	0.55, 0.52	0.28, 0.26	0.83, 0.78
				0.53, 0.46	0.28, 0.25	0.81, 0.72
CA2	10	0.236 + 0.230 (0.466)	4	ND [e], ND	ND, ND	ND, ND
				2.04, 1.43	0.24, 0.20	2.28, 1.63
			7	0.62, 0.51, 0.58	0.10, 0.10, 0.11	0.73, 0.62, 0.69
				0.39, 0.40	0.08, 0.08	0.47, 0.47
NJ	2	0.249 + 0.248 (0.497)	4	1.25, 0.90	0.66, 0.66	1.91, 1.56
				1.20, 0.88	0.68, 0.56	1.88, 1.44
			7	0.93, 0.82	0.86, 0.73	1.80, 1.55
				1.08, 0.96	0.95, 0.82	2.03, 1.78
MI	5	0.250 + 0.260 (0.510)	4	0.82, 1.10	0.67, 0.85	1.50, 1.96
				0.86, 1.00	0.78, 0.82	1.64, 1.81
			7	0.62, 0.63	0.78, 0.70	1.39, 1.33
				0.70, 0.83	0.80, 0.87	1.50, 1.70
NC	2	0.248 + 0.268 (0.516)	4	0.46, 0.47	0.32, 0.34	0.78, 0.81
				0.46, 0.42	0.27, 0.28	0.74, 0.70
			7	0.31, 0.33, 0.21, 0.31	0.27, 0.34, 0.22, 0.35	0.58, 0.67, 0.43, 0.67
				0.35, 0.28	0.36, 0.31	0.71, 0.58

[a] PTI = Post-treatment Interval (days).

[b] Expressed as clethodim. Values represent duplicate or triplicate analyses of two samples from each test.

[c] Acronyms for the dimethyl esters of 3-[2-(ethylsulfonyl) propyl]pentanedioic acid and 3-[2-(ethylsulfonyl)propyl]-3-hydroxypentanedioic acid, respectively.

[d] Total rate depicted in parentheses

[e] ND = Nondetectable; sample was rejected because it was the only treated sample with nondetectable residues.

HED Comments/Conclusions:

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The submitted strawberry residue data and geographic representation are adequate to satisfy the requirements described in OPPTS 860.1500. Seven strawberry field trials were conducted in CA(2), FL (1), MI (1), NJ (1), NC (1), and WA (1). Combined residues of clethodim were 0.42-2.28 ppm in/on strawberry samples harvested 3-4 days after the last of two applications of clethodim (0.94 lb/gal EC) at 0.230-0.268 lb ai/A/application, at 13- or 14-day RTIs, for a total of 0.47-0.50 lb ai/A/season (~1x the maximum proposed rate). These data indicate that the proposed 5.0 ppm tolerance for residues of clethodim and its metabolites in/on strawberry is too high, and that a tolerance of 3.0 ppm would be appropriate. Therefore, the petitioner must submit a revised Section F proposing a tolerance of 3.0 ppm for residues of clethodin and its metabolites in/on strawberries.

OPPTS GLN 860:1520: Processed Food/Feed

There are no regulated processed food or feed items derived from the commodities associated with this petition; therefore, a discussion of tolerances for processed commodities is not relevant.

OPPTS GLN 860.1480: Meat/Milk/Poultry/Eggs

No ruminant and poultry feeding studies were submitted with this petition. Ruminant and poultry feeding studies were previously submitted and reviewed (PP#9F3743, MRIDs 41030221 & 41030222, M. Nelson, 05/12/1990). Permanent tolerances for livestock and poultry have been established for the combined residues of clethodim[(E)-(±)-2-[1-[[(3-chloro-2-propenyl)oxy]imino]propyl]-5-[2-(ethylthio)propyl]-3-hydroxy-2-cyclohexen-1-one] and its metabolites containing the 5-[2-(ethylthio)propyl]cyclohexene-3-one and 5-[2-(ethylthio)propyl]-5-hydroxycyclohexene-3-one moieties and their sulphoxides and sulphones (40 CFR §180.458).

Dairy Cattle

The petitioner conducted a feeding study with lactating dairy cows (MRID 41030222). Fourteen Holstein cows were used for the study (randomly divided into one control group of two cows and three test groups of four cows each). Following an acclimation period of 7 days, each cow in the test groups was given an oral dose of a 5:95 mixture of clethodim:clethodim sulfoxide contained in a gelatin capsule, once daily for 28 consecutive days. The dosing levels were 10 ppm, 30 ppm, and 100 ppm in the diet for the three test groups based on the highest daily food consumption, determined during the acclimation period: 85 lbs/cow/day. **These dosing levels would be equivalent to 0.7x, 2x and 7x the theoretical maxium dietary burden for beef cattle, and 0.64x, 2x and 6.4x the theoretical maxium dietary burden for dairy cattle (based on the current theoretical maximum daily dosage levels).**

Three cows from each dose level and one control cow were sacrificed on test day 29, within 24 hours of the last dose; and the remaining cow in each group on day 31, after 2 days withdrawal. Samples of liver, kidney, composite muscle, and composite fat (peritoneal and subcutaneous) were collected from each carcass for residue analysis.

Milk samples, consisting of equal parts of morning and evening milkings for a given day, were collected from each cow on days -1, 1, 2, 4, 7, 12, 16, 20, 24, 28, 29, 30, and 31.

All tissue and milk samples were maintained under frozen storage (-20°C) until analysis for total clethodim residues (measured as DME, DME-OH, and S-DME, expressed as clethodim equivalents) by a modified version of RM-26A (adapted for milk and bovine tissues). The results of residue analysis of bovine tissues and milk are summarized in Table 13.

Table 13. Clethodim Residues in Dairy Cows

Feeding Levels	Chemicals	Milk	Liver	Kidney	Muscle	Fat
10 ppm	DME	ND	0.06	0.05	ND	ND
	DME-OH	ND	ND	ND	ND	ND
	S-MEDME	ND	ND	ND	ND	ND
30 ppm	DME	0.03	0.12	0.17	ND	0.05
	DME-OH	ND	ND	ND	ND	ND
	S-MEDME	ND	ND	ND	ND	ND
100 ppm	DME	0.08	0.45	0.54	0.07	0.15
	DME-OH	ND	ND	ND	ND	ND
	S-MEDME	0.03	0.09	0.08	ND	ND

ND = Not Detected (<0.0125 ppm for milk and <0.05 ppm for tissues)

DME residues were found in liver and kidney at all feeding levels, in milk and fat at the 30 and 100 ppm feeding levels, and in muscle at the 100 ppm level only. S-DME was found in milk, liver, and kidney at the 100 ppm level. DME-OH was not found in milk or any tissue at any feeding level. Residues in milk plateaued on test days 1 or 2.

No detectable residues of DME, DME-OH, or S-DME were reported in any control milk (<0.0125 ppm) or bovine tissue (<0.05 ppm) samples.

Composite whole milk samples collected on test days 25, 26, and 27 from the control group and the 100 ppm dose level group were processed to obtain skim milk (nonfat solids), cream (fat solids), pasteurized milk, and acid whey (lactose). Analysis for total clethodim residues (DME + DME-OH + S-DME) was performed on these processing fractions. Based on the recommended tolerances in this submission and established tolerances, the maximum theoretical residues in diets of beef and dairy cattle were calculated and the current theoretical maximum daily dosage levels were determined (see Table 14).

Table 14. Theoretical dietary burden of clethodim from various feed commodities for beef and dairy cattle

Feed Commodity	Tolerance or Proposed Tolerance (ppm)	% Dry Matter	Beef Cattle		Dairy Cattle	
			% of Diet	Burden (ppm)	% of Diet	Burden (ppm)
Peanut hay	3.0	85	25	0.88	40	1.41
Alfalfa hay	6.0	35	30	5.14		
Colver hay	20	89	30	6.7	60	13.5
Soybeans	10.0	89	15	1.69		
Total			100	14.41	100	14.91

HED Comments/Conclusions:

The established tolerances on meat and milk are adequate to cover the proposed uses. According to Table 1 of OPPTS 860.1000 and the recommended and established tolerances for clethodim, the maximum theoretical dietary burdens were determined to be 14.41 ppm and 14.91 ppm for beef and dairy cattles, respectively. Based on the previous feeding studies, the secondary residues in meat and milk will not exceed the established tolerances.

As there are no poultry feed items associated with the current petition, no secondary residues are expected to occur in poultry tissues and eggs.

OPPTS GLN 860.1850 and 860.1900: Confined/Field Accumulation in Rotational Crops

A confined rotational crop study of [ring-4,6-^{14}C]-clethodim with carrots, lettuce, and wheat (MRID 41030211) was conducted. The study was reviewed by E. B. Conerly (EFGWB Science Chapter for Clethodim, 06/26/1990). Results indicated that there is no need for field rotational crop trials. A 1- month plantback interval for crops rotated with alfalfa was specified (D 236382, M. Collantes, et. al, 2/10/98). The use directions submitted with the current petition do not specifically address rotational crops. The directions for use on fallow or nonproducing agricultural land state do not plant any crop for 30 days after application unless clethodim is registered for use on that crop.

International Harmonization of Tolerances

There are no established Codex maximum residue limits (MRLs) for residues of clethodim in/on the commodities discussed in the subject petition; therefore, there are no questions with respect to Codex/U.S. tolerance compatibility. Codex MRLs are currently established on various crop and livestock commodities in terms of the sum of clethodim and its metabolites containing 5-(2-ethylthiopropyl)cyclohexene-3-one and 5-(2-ethylthiopropyl)-5-hydroxycyclohexene-3-one moieties and their sulphoxides and sulphones, expressed as clethodim.

cc: RF, PP# 0E06097, Mxue, PM# 23, MRust
RDI: ChemTeam:10/25/2000 :Sdapson 10/25/2000
7509C: RAB3, MXue :CM-2: RM 810F: 703 305-6198: 10/25/2000

AGENCY MEMORANDA CITED

CBTS No.:	12468
DP Barcode:	D194694
Subject:	PP# 9F3743 Clethodim (Select®) in/on Soybeans, Cottonseed, and Animal Commodities. Evaluation of the Revised Compound Specific Residue Analytical Method, EPA-RM-26D-2, and the New Supporting Independent Laboratory Validation Data.
From:	F. Griffith
To:	J. Miller/D. Marlow/A. Kocialski
Dated:	9/29/93
MRID(s):	None

CBTS Nos.:	13703, 13704, and 13705
DP Barcode:	D203378
Subject:	4F4340. Clethodim in/on Sugar Beets and Onions (Dry Bulb). Evaluation of Residue Data and Analytical Methodology.
From:	J. Morales
To:	J. Miller/D. Kenny
Dated:	2/8/95
MRID(s):	43166400, 43166402, and 43166403-43166407.

CBTS Nos.:	16157, 16158, and 16442
DP Barcodes:	D219077, D219078 and D220698
Subject:	5F4572/5H5729. Clethodim in/on Tomatoes and Tuberous and Corm Vegetables. Evaluation of Residue Data and Analytical Methodology.
From:	J. Morales
To:	J. Miller/D. Kenny
Dated:	2/8/96
MRID(s):	43757701-43757704

CBTS Nos.: None
DP Barcodes: D258351
Subject: OR990045. Clethodim. Section 24(c): Clover Grown for Seed.
From: L. Cheung
To: D. Kenny/ J. Miller
Dated: 9/9/99
MRID(s): None