



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

AUG 17 1989

OFFICE OF  
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: PP#8F3658. Triasulfuron on Wheat and Barley.  
Amendment of May 3, 1989 and Method Trial Report.  
MRID 410879-01  
HED No. 9-1494  
DEB No. 5361, 5362

FROM: Martha J. Bradley, Chemist *MJ Bradley*  
Dietary Exposure Branch  
Health Effects Division (H7509C)

TO: Robert Taylor, PM 25  
Herbicide-Fungicide Branch  
Registration Division (H7505C)

and  
Toxicology Branch  
Fungicide Herbicide Support  
Health Effects Division (H7509C)

THRU: Richard D. Schmitt, Ph.D., Chief  
Dietary Exposure Branch  
Health Effects Division (H7509C)

*R. Lorange for RDS*

A new chemical review was completed for this chemical on the subject crops (memo 6/22/89) and the petition is in reject status.

Ciba-Geigy Corporation has amended the directions for use for the Amber herbicide, triasulfuron (3-(6-methoxy-4-methyl-1,3,5-triazin-2-yl)-1-[2-(2-chloro-ethoxy)-phenylsulfonyl]-urea, CGA-131036) in or on wheat and barley to include a preemergent application. The purpose of this data package is to submit the supporting residue data for the amended use.

The second method trial for a lower level residue in wheat and barley grain at 0.01 ppm has been completed and the results are also discussed in this review.

## Summary of Deficiencies remaining to be resolved

New Directions for use

Analytical methodology

New Tolerance proposals

### Conclusions

1. The label indicates under "Precautions" that two applications may be made, separated by at least 60 days. The directions for use of the product do not give any instruction in regard to the split application. Include complete directions for this type of use. Limit the application to winter wheat and barley or submit information to indicate that two applications are possible for spring planted wheat and barley by boot stage. The directions should indicate when to use split application as opposed to the single application or indicate conditions when split applications would be made. The split application dosage rates should also be included in the section under "Rates to Use".

2a. Methods AG-500 and AG-508 should be revised to include the modifications used by the Analytical Chemistry Branch as stated in L. Cheng memo of March 23, 1989, PP#7G3551.

Note to PM: A copy of this memo is attached to be forwarded to Ciba Geigy so that the modifications can be incorporated in the methods.

Method AG-500 should also be revised to include the modifications to allow for a detection limit of 0.01 ppm in wheat and barley grain.

2b. The petitioner should show that triasulfuron can be quantitated in the presence of the pesticides in group VII of the specificity study.

3. Tolerance proposals for triasulfuron residues of 2 ppm in wheat and barley forage and 15 ppm in wheat and barley hay should be submitted.

### Recommendation

DEB recommends against the proposed tolerances for triasulfuron on wheat, barley, meat and milk because of Conclusions 1 (directions for use), 2a and 2b (methodology), and 3 (more appropriate tolerances). For further consideration of this petition, the deficiencies listed in the above Conclusions should be resolved.

## Detailed Considerations

### Proposed New Use

The preemergence application for wheat is for the control of Italian ryegrass only. Amber is not to be applied for preemergence use to late fall-seeded wheat (after November 1) since crop injury may result. The application rates are the same as for the postemergent uses discussed in our (M. Bradley) review of 6/22/89.

### Directions for Use

After consultation with C. Grable of Registration Division, the following comments are offered for the present labeling. The label indicates under "Precautions" that two applications may be made, separated by at least 60 days. The directions for use of the product do not give any instruction in regard to the split application. Include complete directions for this type of use. Limit the application to winter wheat and barley or submit information to indicate that two applications are possible for spring planted wheat and barley by boot stage. The directions should indicate when to use split application as opposed to the single application or indicate conditions when split applications would be made. The split application dosage rates should also be included in the section under "Rates to Use".

### Residue Data for New Preemergence Use

#### Storage Stability of Residues

Triasulfuron residues are essentially stable in wheat forage, straw, and grain under freezer storage conditions (-15°C) for up to 24 months. The samples from the preemergence use were stored for no more than 18 months before analysis.

#### Residue Studies

Four field studies were conducted for spring wheat and eight studies for winter wheat in the states of California, Kansas, Minnesota, Nebraska, North and South Dakota, North Carolina, Ohio, Oklahoma, Texas, and Washington. A single application of 24.5 g ai/A (1X rate) or 49 g ai/A (2X rate) was made preemergence, nonincorporated, broadcast with the 75WG or 50T formulation. Forage samples were taken 58 to 190 days after treatment while straw and grain samples were taken at normal harvest, 113 to 338 days after treatment. Some forage samples were air dried for hay samples.

No detectable residues (<0.01 ppm for grain, <0.05 ppm for the rest) were found in any samples from the 1X or 2X applications. The method used was AG-500 which has had successful trials for wheat grain and straw. Recoveries from fortifications of 0.01 to 0.5 ppm in wheat forage, hay, straw and grain ranged from 65 to 113% with a mean of 84 to 87%.

The new preemergence use does not change our previous conclusions on residue levels expected from the combined uses.

An analysis of all the 1X forage residue data (from all submissions) show that a 2 ppm tolerance for forage with a 7 day pre harvest interval (PHI) would be more appropriate than the proposed 1 ppm tolerance.

A proposed tolerance of 15 ppm is needed for wheat and barley hay to reflect a 7 fold increase in residue level for forage, (2 ppm) at 7 days PHI, dried to hay.

Residue levels are not expected to exceed the proposed tolerances of 0.02 ppm on wheat and barley grain and of 2 ppm on wheat and barley straw.

#### Method Trial Results

The second method trial report, dated July 14, 1989 for wheat grain has been received. The trial was conducted to test a modification of method AG-500 consisting of a change in the concentration of the final extract and injection volume. The addendum to the analytical method allows for a detection limit of 0.01 ppm in wheat and barley grain.

Wheat grain was fortified in duplicate, with 0.01 and 0.02 ppm triasulfuron. Recoveries were 95 to 105% with a control of <0.01 ppm. No modifications, other than those previously reported, were needed. Sample chromatograms and calculations are also included.

Methods AG-500 and AG-508 should be revised to include the modifications used by the Analytical Chemistry Branch as stated in L. Cheng memo of March 23, 1989, PP#7G3551. Method AG-500 should also be revised to include the modifications to allow for a detection limit of 0.01 ppm in wheat and barley grain.

DEB concludes that adequate analytical methodology is available to enforce the proposed tolerance provided that only the parent compound is to be regulated; that triasulfuron can be quantitated in the presence of the pesticides in group VII of the specificity study; and that methods AG-500 and AG-508 are suitably revised and submitted.

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Attachment 1: Memo L. Cheng, March 23, 1989

cc without Attachment: PP8F3658, M. Bradley, RF, Circulate (7),  
PMSD/ISB

H7509C:DEB:M Bradley:mb:CM#2:Rm810:557-7324:08/15/89

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

MAR 23 1989

MEMORANDUM

OFFICE OF  
PESTICIDES AND TOXIC SUBSTANCES

SUBJECT: PP7G3551 & 100-EUP-ON. Triasulfuron on Wheat and Barley. Evaluation of Analytical Methods. ACB Report dated 2/14/89. No MRID #. No DEB #.

FROM: Leung Cheng, PhD, Chemist *L. Cheng*  
Special Registration Section II  
Dietary Exposure Branch  
Health Effects Division (TS-H7509C)

THRU: Francis Suhre, Acting Section Head *Francis Suhre*  
Dietary Exposure Branch  
Health Effects Division (TS-H7509C)

TO: Robert Taylor, PM 25  
Fungicide-Herbicide Branch  
Registration Division (TS-H7505C)

The Environmental Chemistry Section of the Analytical Chemistry Branch has completed method validation studies for triasulfuron in or on wheat (grain and straw), meat (muscle and kidney) and milk, as requested by DEB (memo of 2/23/88). The methods tested were:

1. # AG-500. CGA-131036 - Analytical Method for Crops. Determination of Residues by High Performance Liquid Chromatography with Column Switching, and
2. # AG-508. CGA-131036 - Analytical Method for Tissues, Milk and Eggs. Determination of Residues by High Performance Liquid Chromatography with Column Switching.

1) # AG-500

Method Summary

Crop samples of wheat (barley) grain, forage or straw are extracted by homogenization in methanol containing ca 5% water and 0.5% phosphoric acid. After filtration, an aliquot of the extract is diluted with water and CGA-131036 residues are partitioned into methylene chloride. The residues are further

cleaned up by means of a Bond Elute CN column prior to analysis by column switching HPLC with two columns (Lichrosorb CN and Zorbax ODS) and ultraviolet detection (232 nm). The amount of CGA-131036 in the unknown sample is determined by comparing the peak height or area for the unknown sample with the standard curve generated from known concentrations of CGA-131036.

### Results

The results of the method validation for triasulfuron in wheat grain and straw are as follows:

| <u>Commodity</u> | <u>Chemical Added</u> | <u>PPM Added</u> | <u>PPM Found</u> | <u>% Recovery</u> |
|------------------|-----------------------|------------------|------------------|-------------------|
| Wheat grain      | CGA-130136            | 0                | <0.05            | -                 |
|                  | "                     | 0.100            | 0.105            | 105               |
|                  | "                     | 0.100            | 0.079            | 79                |
|                  | "                     | 0.500            | 0.435            | 87                |
|                  | "                     | 0.500            | 0.385            | 77                |
| Wheat straw      | "                     | 0                | <0.10            | -                 |
|                  | "                     | 0.500            | 0.370            | 74                |
|                  | "                     | 0.500            | 0.386            | 77                |
|                  | "                     | 1.000            | 0.696            | 70                |
|                  | "                     | 1.000            | 0.702            | 70                |

ACB reported the method was slightly modified as follows:

"HPLC Mobile Phase Flow Rate (Table VII, page 19) - after HPLC column switching, the mobile phase showed a peak which preceded and overlapped the analytical peak at the listed flow rates of mobile phase at 1.0 ml/min. The flow rate of mobile phase #2 was modified to 0.5 ml/min to reduce the overlapping. At this flow rate, the separation of the interfering peak, about 1 min apart from the analytical peak, was adequate for the peak height measurements."

## 2) #AG-508

Method Summary

Samples (except milk) are extracted by homogenization in methanol containing ca 5% water and 0.5% phosphoric acid. An aliquot of the filtrate is removed and the methanol is evaporated for kidney samples but not for meat and liver. After diluting the tissue aliquot with water, CGA-131036 is partitioned into methylene chloride and further cleaned up on a Bond Elut CN column.

For milk, samples are extracted by homogenizing in acetonitrile containing ca 5% water and 0.5% phosphoric acid. An aliquot is removed after filtration and diluted with water and saturated sodium chloride solution. CGA-131036 residues are partitioned into methylene chloride.

CGA-131036 residues are determined by column switching HPLC with two columns (Lichrosorb CN and Zorbax ODS) and ultraviolet detection (232 nm). The amount of CGA-131036 in the unknown sample is determined by comparing the peak height or area for the unknown sample with the standard curve generated from known concentrations of CGA-131036.

Results

The results of the method validation for triasulfuron in milk, and beef tissue (muscle and kidney) are as follows:

| <u>Commodity</u> | <u>Chemical Added</u> | <u>PPM Added</u> | <u>PPM Found</u> | <u>% Recovery</u> |
|------------------|-----------------------|------------------|------------------|-------------------|
| Milk             | CGA-130136            | 0                | <0.01            | -                 |
|                  | "                     | 0.01             | 0.008            | 80                |
|                  | "                     | 0.01             | 0.008            | 80                |
|                  | "                     | 0.05             | 0.038            | 76                |
|                  | "                     | 0.05             | 0.034            | 68                |
| Beef muscle      | "                     | 0                | <0.04            | -                 |
|                  | "                     | 0.05             | 0.037            | 74                |
|                  | "                     | 0.05             | 0.050            | 100               |
|                  | "                     | 0.10             | 0.069            | 69                |
|                  | "                     | 0.10             | 0.065            | 65                |

| <u>Commodity</u> | <u>Chemical Added</u> | <u>PPM Added</u> | <u>PPM Found</u> | <u>% Recovery</u> |
|------------------|-----------------------|------------------|------------------|-------------------|
| Beef kidney      | "                     | 0                | <0.04            | -                 |
|                  | "                     | 0.50             | 0.374            | 75                |
|                  | "                     | 0.50             | 0.346            | 69                |
|                  | "                     | 1.00             | 0.850            | 85                |
|                  | "                     | 1.00             | 0.850            | 85                |

ACB reported the method was slightly modified as follows:

1) "HPLC Mobile Phase Flow Rate (Table I, page 15) - after HPLC column switching, the mobile phase showed a peak which preceded and overlapped the analytical peak at the listed flow rates of 1.0 ml/min. The flow rate of mobile phase #2 was modified to 0.5 ml/min to reduce the overlapping. At this flow rate, the separation of the interfering peak, about 1 min apart from the analytical peak, was adequate for the peak height measurements."

2) "Milk extraction (step 5.1.3.3, page 10) - the filtration through Reeve Angel 802 and Whatman 2V filter paper by gravitation was very slow (about 1 drop per minute). Vacuum filtration was applied using a 7-cm Buchner funnel and Whatman #1 filter paper."

### CONCLUSIONS

1. Method # AG-500 is adequate for enforcement purposes. The method is capable of determining triasulfuron residues (parent) in or on wheat and barley at 0.1 ppm, provided the modifications suggested by EPA's laboratory are incorporated. A copy of the revised method should be provided to the Agency.

2. Method # AG-508 is adequate for enforcement purposes. The method is capable of determining triasulfuron residues (parent) in or on meat, meat byproducts, fat and milk of cattle at 0.01-0.05 ppm, provided the modifications suggested by EPA's laboratory are incorporated. A copy of the revised method should be provided to the Agency.

3. If it becomes necessary to include additional metabolites as a result of a permanent tolerance petition review, the petitioner would need to develop suitable enforcement methods for these metabolites.

RECOMMENDATION

DEB recommends that the publication of methods # AG-500 and # AG-508 be deferred until permanent tolerances for wheat and barley are established.

Attachment: ACB report of 2/14/89

cc(with Attachment):PM 25

cc(without Attachment):Circ, RF, PP7G3551, Cheng, M. Bradley, PMV/MTO F, R. Schmitt (Acting Chief), PMSD/ISB

RDI:FSuhre:3/22/89:EZager:3/22/89:

TS-H7509C:DEB:CM#2:Rm810:Cheng:3/20/89:1:3/22/89