PM SD ISB

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

WASHINGTON, DC 20460

FEB 8 1989

OFFICE OF
PESTICIDES AND
TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: PP#2F2677 Sencor (Metribuzin) in or on Soybeans - Amendment of July 7, 1988 to Review Additional Soybean Residue Data Submitted in Response to the Metribuzin Registration Standard Data Requirements (MRID No. 402779-04) DEB No. 4579

FROM: Martin F. Kovacs, Jr., Ph.D., Chemist
Tolerance Petition Section II
Dietary Exposure Branch
Health Effects Division (TS-769C)

TO: Robert J. Taylor, PM 25
Fungicide-Herbicide Branch
Registration Division (TS-767C)

and

Toxicology Branch II
Herbicide, Fungicide and Antimicrobial Support
Health Effects Division (TS-769C)

THRU: Richard D. Schmitt, Ph.D., Acting Chief
Dietary Exposure Branch
Health Effects Division (TS-769C)

Background

The current tolerance established for combined residues of metribuzin and its triazinone metabolites in or on soybeans is 0.1 ppm (40 CFR 180.332). On April 6, 1982, Mobay petitioned the Agency for an increase in the tolerance for soybeans to 0.2 ppm to support the use of metribuzin in postemergence applications (PP#2F2677). In a letter dated August 10, 1982, R. Taylor, PM 25 (RD) noted that an increase in the soybean tolerance to 0.25 ppm was needed because residues from the postemergence use would exceed the proposed 0.2 ppm tolerance at 70 days after application. On March 21, 1983, Mobay amended Section F of the petition to propose a tolerance of 0.25 ppm for combined residues of metribuzin and its triazinone metabolites in or on soybeans. In DEB's M.F. Kovacs, Jr. January 25, 1984 review of the November 3, 1983

amendment to PP#2F2677, DEB recommended for the proposed increase in the tolerance for residues of the herbicide Sencor and its triazinone metabolites in or on soybeans to a level of 0.25 ppm.

In a letter dated July 23, 1985, R. Taylor PM 25 (RD) informed the petitioner that the Agency could not grant the proposed increase in the tolerance for soybeans pending resolution of the toxicological deficiencies cited in the Metribuzin Registration Standard Guidance Document dated June 28, 1985. In the Metribuzin Registration Standard Guidance Document, the Agency also required data from the Mississippi delta area showing residues in soybeans harvested at normal maturity following two postemergence applications of Sencor 4 or Sencor DF at 0.5 lb ai/A made at 7-day intervals preceded by a preemergence application at 1.0 lb ai/A and a preplant application at 0.75 lb ai/A.

Summary of Deficiencies Remaining to Be Resolved

The petitioner will need to revise Section F to increase the tolerance for residues of the herbicide Sencor and its triazinone metabolites in or on soybeans from 0.1 to 0.3 ppm.

Recommendations

DEB will recommend for the establishment of a metribuzin tolerance on soybeans provided that it is proposed at a 0.3 ppm level in a Revised Section F.

Conclusions

1. Adequate analytical methodology was available to generate residue data for metribuzin and its triazinone metabolites on soybeans, soybean forage, and soybean hay, submitted in the MS delta trial.

2. Soybean sample storage stability data were not submitted by the petitioner to support frozen residue samples held for approximately 1 year in the MS delta trial. These data were required for all new residue studies submitted in conjunction with the Metribuzin Registration Standard (December 20, 1984 Residue Chemistry Chapter). However, DEB will forego additional storage stability data for soybeans since the current tolerance request only deals with an appropriate increase of the existing tolerance on soybeans rather than the establishment of an initial tolerance on soybeans.

3. The submitted MS delta soybean residue data reflected a maximum residue of 0.14 ppm following less than a complete treatment schedule (3 vs. 4 treatments) and/or maximum recommended application rates for all treatments at the minimum recommended PHI. The maximum application made totaled 2.125 lb ai/A/season (0.77X) vs. the maximum 2.750 lb ai/A/season recommended on the current label for the MS delta region. However, DEB calculates that if a full treatment schedule was followed in the MS delta trial (2.750 v. 2.125 lb ai/A/season), maximum residues on soybeans should not exceed 0.3 ppm.

4. Because of conclusions 2 and 3 above, DEB now reconsidered its previously favorable recommendation made in the M.F. Kovacs, Jr. January 25, 1984 review of PP#2F2677 to increase the tolerance for residues of the herbicide Sencor and its triazinone metabolites in or on soybeans from 0.1 to 0.25 ppm. The variability of residue data from the MS delta region, which reflects the maximum label treatment schedule and rates permitted for all soybean production areas in the United States dictates that a tolerance proposal of 0.3 ppm would now be more appropriate to cover maximum residues of Sencor and its triazinone metabolites resulting from all geographical use patterns.

5. The Canadian tolerance of 0.1 ppm (NR) for Sencor parent compound only is incompatible with the 0.25 ppm proposed in this petition for combined residues of Sencor and its triazinone metabolites.

Present Considerations

In the current submission (amendment to PP#2F2677) the petitioner has requested that his proposal to increase the tolerance for soybeans from 0.1 to 0.25 ppm be reactivated since both the toxicological deficiencies cited in the Registration Standard and the residue chemistry deficiencies cited in DEB's January 24, 1984 review have been resolved.

The current amendment consists of three cover letters dated July 24 and August 3, 1987, and July 7, 1988 from John S. Thornton, Manager Registrations Research and Development, Mobay Corporation Agricultural Chemicals Division to Robert J. Taylor, PM 25 (EPA/RD), a revised title page, table of contents, and Sections D and G. The two sections of the petition have been revised as follows:

- Section D has been revised to include Accession Numbers assigned to soybean processing data submitted

on March 21 and November 3, 1983, and to include a citation to the new soybean residue study (Mobay Report No. 94737) submitted in accordance with requirements of the Registration Standard Guidance Document.

- Section G has been edited to clarify the statements relative to time of submission of the processing study for soybeans and to include referral statements for the additional residue data which substantiate the need for the tolerance increase for soybeans.

The specific data gap pertaining to additional soybean residue studies cited in footnotes 12 and 16 (Table A Generic Data Requirements for Metribuzin) of the Metribuzin Registration Standard Guidance Document dated June 28, 1985 is restated below followed by the petitioner's response and DEB's comments.

Metribuzin Registration Standard Guidance Document June 28, 1985 Table A Section 158.125 Residue Chemistry

12/Data reflecting residues in or on soybeans harvested at normal maturity following two postemergence applications made at 7-day intervals of the 75% WP or 4 lb/gallon FLC formulation at 0.5 lb ai/A application which were preceded by a preemergence application at 1 lb ai/A and a preplant application at 0.75 lb ai/A. Tests must be conducted in the MS delta region.

16/Data reflecting combined residues of metribuzin, DADK, DA, and DK in or on soybean forage and hay harvested 40 days after the last of two postemergence applications of a WP or 4 lb/gal FLC formulation at 0.5 lb ai/A preceded by a preemergence application at 1 lb ai/A and a preplant application at 0.75 lb ai/A. Tests must be conducted in the MS delta region.

Petitioner's Response

DEB Note: Although the new soybean residue study cited below was submitted in accordance with the Registration Standard Guidance Document and not for the stated purpose of

supporting the tolerance proposal in PP#2F2677, it will be evaluated by DEB in this review for the purpose of supporting the tolerance proposal.

> Mobay Report No. 94737 "SENCOR - Magnitude of Residue on Soybeans." Guidelines Reference No. 171-4 Crop Field Trials, by W.W. Loeffer, Mobay Corporation (Analyses by Morse Laboratories, Inc.) dated July 21, 1987 (MRID No. 402779-04)

Analytical Method

"The procedure consisted of an initial reflux with a 4:1 acetonitrile:water solvent mixture to release 'Bound' (Conjugated) residues of SENCOR and metabolites. Following a filtration step, acetonitrile was removed by evaporation. SENCOR and metabolite residues were separated from each other by liquid-liquid partition. The SENCOR fraction of the extract was further cleaned up using a Silica-gel column. Conditions were described for the separation of DADK from the crop extractives that resulted in the least interferences during the gas chromatographic procedure, thus expediting the analysis of large numbers of residue samples. Alternate Silica-gel column procedures were described for determining DA and DK residues if desired. Final residue determination for SENCOR and metabolites was by electron capture detection."

With this method, reported control values for Sencor, DADK, DK, and DA residues in soybeans, soybean forage, and soybean hay (dry vines) were < 0.01 to 0.02, < 0.01, and 0.01 to 0.02 ppm, respectively. Submitted chromatograms confirm these control (limit of determination) values.

Recovery values for each of Sencor and its metabolites (DADK, DK, and DA) from soybeans, soybean forage and soybean hay when fortified at 0.01 to 0.05 ppm were 70 to 120%, X = 83%; 60 to 110%, X= 85%; and 60 to 120%, X= 88%, respectively.

Residue Data

Two 1986 field trials were conducted in Louisiana utilizing the 75 DF Formulation and two 1986 trials were conducted in Mississippi utilizing the 4 Flowable formulation. Two different treatment patterns were employed at each location:

1. Three treatments, the first of which is a preemergence application at a rate of 16 oz ai/A, followed by two postemergence directed foliar

applications at a rate of 8 oz ai/A. There was a 7-day interval between the postemergence applications.

2. Four treatments, the first of which was a preplant treatment at a rate of 10 oz ai/A followed by a preemergence application at a rate of 8 oz ai/A. The third and fourth applications were postemergence directed foliar applications made 7 days apart at a rate of 8 oz ai/A.

Green forage was sampled at approximately 40 days posttreatment, and dry beans and dry vines were sampled at harvest (79 to 89) and (79 to 95) days posttreatment, respectively.

Total Sencor residues (SENCOR + DADK + DK + DA) on soybeans, soybean forage, and soybean hay following 3 or 4 applications were: (0.03, 0.06/0.03, 0.14), (< 0.01, 0.08/0.02, 0.12) and (0.10, 0.21/0.19, 0.19) ppm, respectively. DADK was the predominant residue in soybeans and soybean hay samples whereas DADK and Sencor residues predominated in soybean forage samples.

All of the residue values reported were gross (apparent) residues of Sencor and its metabolites and are uncorrected for controls or for recoveries of approximately 83 percent on soybeans, 85 percent on soybean forage, and 88 percent on soybean hay (dry vines).

DEB's Comments

Analytical Method

The analytical method used by the petitioner to generate the submitted metribuzin residue data is similar to one which was subjected to a successful method trial in conjunction with PP#2F1274. The method is judged adequate by DEB to generate metribuzin residue data on soybeans, soybean forage, and soybean hay.

Storage Stability Data

The petitioner states that samples involved in this study were held a maximum of 297 days in frozen storage before analysis. DEB calculates a maximum frozen storage interval of 313 to 349 days between sample harvest and analysis.

The Residue Chemistry Chapter (Storage Stability Data) of the December 20, 1984 Metribuzin Registration Standard requires that any additional data requested in the Standard

be generated from samples stored (frozen) no longer than 2 weeks prior to analysis. However, the Registration Standard also documents storage stability recovery data at -18 to -23 °C for Sencor and DADK for tomatoes (1024 to 1063 days), green peas (761 days), potatoes (320 to 358 days), and green alfalfa (355 days) at (72 to 75/58 to 59) (76/65), (107/69) and (100/70 to 108%) respectively. Recovery of Sencor and DADK from soybeans stored at -18 °C for only 46 days was 65 and > 100 percent, respectively. Based on the aforementioned data on crops other than soybeans, DEB is not raising any serious questions regarding the integrity of soybean residue samples obtained in the submitted MS delta residue trials. However, since residue decline in soybeans per se has not been reported over a 1-year storage interval, the reported residue data must be adjusted slightly upward to reflect potential residue decline during storage.

Residue Data (MS Delta Trials)

The number and/or rate of preplant and preemergent treatments to MS and LA soybeans and the PHIs observed were at variance with the requirements of the Metribuzin Registration Standard. For example, in two of the four trials submitted, the preplant application at 0.75 lb ai/A was omitted and the remaining two trials reflected the four recommended applications (preplant, preemergent, postemergent, postemergent) but at 0.83X, 0.5X, 1X, and 1X the maximum label rate, respectively, for the MS delta region. The PHIs reported for soybeans and soybean hay (79 to 89) and (79 to 95 days), respectively, were greater than the 70 days recommended whereas the reported average 41.5-day PHI for soybean forage approximated the 40 days recommended.

DEB agrees with the petitioner that the submitted residue data from the MS delta (reflecting a maximum residue of 0.14 ppm on soybeans following four applications totaling 2.125 lb ai/A/season or 0.77X the total 2.750 lb ai/A/season recommended on the current label) substantiate the need for the requested tolerance increase for soybeans from 0.1 to a more appropriate higher level. Based on the currently submitted MS delta residue data reflecting less than a complete treatment schedule and/or maximum recommended application rates for all treatments at the minimum recommended PHI inadequately supported by sample storage stability data at approximately 1 year, DEB has now reconsidered its previously favorable recommendation made in the M.F. Kovacs, Jr., January 25, 1984 review of PP#2F2677 to increase the tolerance for residues of the herbicide Sencor and its triazinone metabolites in or on soybeans from 0.1 to 0.25 ppm.

Because of the variability and slight adjustments needed for the MS delta residue data which reflect the maximum label treatment schedule and rates permitted for all geographical areas, DEB now recommends that the petitioner submit a revised Section F proposing a tolerance for residues of the herbicide Sencor and its triazinone metabolites on soybeans at 0.3 ppm.

Other Considerations

An International Residue Limit Status sheet is attached to this review. There is a Canadian tolerance of 0.1 ppm (NR) for Sencor parent compound only which is incompatible with the 0.25 ppm proposed in this petition for combined residues of Sencor and its triazinone metabolites.

Attachment

cc: R.F.,Circu, Reviewer (M. Kovacs), PP#2F2677, Metribuzin Registration Standard File, PMSD/ISB (Eldredge)

RDI:JHOnley:1/24/89:RDSchmitt:edited by fmm:1/24/89

INTERNATIONAL RESIDUE LIMIT STATUS

CHEMICAL Sencor (Metribuzin)

CODEX NO. _____

CODEX STATUS:

No Codex Proposal
Step 6 or above

Residue (if Step 8): _____

Crop(s)	Limit (mg/kg)

PROPOSED U.S. TOLERANCES:

Petition No. 2F2677

RCB Reviewer Martin F. Kovacs, Jr.

Residue: 4-Amino-6-Tert-Butyl-3-(Methylthio)-1,2,4-Triazin-5-(4H)-One and its Triazinone Metabolites

Crop(s)	Limit (mg/kg)
Soybeans	0.25

CANADIAN LIMITS:

No Canadian limit

Residue: Metribuzin

Crop(s)	Limit (mg/kg)
Soybeans	0.1*

MEXICAN LIMITS:

No Mexican limit

Residue: _____

Crop(s)	Limit (mg/kg)

NOTES:

*Negligible residue type limit