PM SD/ISB

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

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MEMORANDUM

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

SUBJECT: PP#8F3683/FAP#8H5563. SENCOR® Herbicide (Metribuzin) in/on Alfalfa Seed, Alfalfa Chaff, Asparagus, Barley Forage, Barley Hay, Corn Silage, Corn Cannery Waste, Pea Straw, Wheat Hay, Tomato Processed Products and Sugarcane Molasses. Storage Stability Study -- Amendment to Our Memo Dated 10/27/89.

MRID # 410206-01. No DEB #.

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Background

In Conclusion #8a of our 10/27/89 memo, we stated

> "Storage stability data are lacking for corn. Mobay must produce data showing that metribuzin residues are stable in corn grain and fodder held in frozen storage for up to 253 days.

The Residue Chemistry Chapter of the Registration Standard has concluded that storage stability of metribuzin and its triazinone metabolites is dependent on the particular matrix.

In a letter dated 2/28/89 (received by HED 10/5/89), Mobay informed EPA that a storage stability study for metribuzin and

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ethiozin metabolites in various biological matrices was being submitted under PP#8F3656 (TYCOR® Ethiozin Herbicide). (Ethiozin, containing an ethylthio group, is virtually identical to metribuzin, which contains a methylthio group. Two of the triazinone metabolites from each herbicide -- DK and DADK -- are identical.) This study is discussed in this memo and Conclusion #8a revised.

In the 10/27/89 review, we inadvertantly omitted a discussion concerning barley. Mobay has proposed tolerances of 2.0 ppm and 7.0 ppm for barley forage and hay, respectively, based on a recommendation of the Registration Standard. We discuss these proposed tolerances in this memo.

Summary of Deficiencies Remaining to Be Resolved

All deficiencies as listed in our 10/27/89 memo must be resolved, with the exception of Conclusion #8a (concerning storage stability). That conclusion should be changed to the following:

> Storage stability data submitted in Mobay Report 98504 as well as earlier data indicate that the stability of metribuzin and the triazinone metabolites DA and DK in frozen matrices varies widely depending on the particular matrix. Therefore, **we require that any additional residue data submitted must either be generated from samples stored frozen no longer than 2 weeks or be accompanied by storage stability data for metribuzin, DA and DK.**
>
> There is no need for a storage stability study on corn when metribuzin is registered only for preemergent use.

Conclusions

Our conclusion concerning storage stability is that given above. Conclusions concerning the residue data reviewed in our earlier memo are not affected by the revision in Conclusion #8a.

The existing tolerance of 1.0 ppm for residues of metribuzin in/on barley straw remains appropriate. There is an error in the Guidance Document of the Registration Standard, which requested that a tolerance of 2.0 ppm be proposed.

The proposed tolerances of 2.0 ppm and 7.0 ppm for metribuzin residues in/on barley forage and hay, respectively, are appropriate.

Recommendation

We continue to recommend against the proposed tolerances for reasons given the following conclusions in our 10/27/89 memo:

Conclusions 1a, 1b (label); 2a, 2b, 2c (plant metabolism); 3a, 3b, 3c (animal metabolism); 4a, 4b, 4c (analytical methods); 5b (wheat processing study); 6b (alfalfa seed use label); 8a (storage stability **as revised in this memo**); 8c (corn processing study).

Detailed Considerations

The study, Mobay Report No. 98504, titled "Stability of Metribuzin and Ethiozin Metabolite Residues in Biological Matrices During Frozen Storage" (MRID # 410206-01), was reviewed by S. Willett in her 9/28/89 New Chemical Review of ethiozin, PP#8F3656. Samples of beef muscle, liver, fat, kidney and milk; chicken liver and eggs; and wheat grain, forage and straw were fortified with ^{14}C-labeled T-DA (which differs from metribuzin metabolite DA only by replacement of the methylthio group with an ethylthio group), DADK, DK and DA. (Names and structures of metribuzin and its triazinone metabolites are given as Attachment 1 in our earlier memo.) In a separate study ^{14}C-labeled ethiozin was also spiked into the above matrices. Fortification levels ranged from 1 to 4 ppm. Samples were stored at -5°C and analyzed at 0, 30, 90, and 270 days and 1 and 2 years. Residues were extracted, and total radioactivity in the extracts was determined by LSC. Compounds present were identified using TLC.

Ms. Willett concluded that "The storage stability data submitted for DK implies that DK is unstable in all commodities tested except eggs, milk and wheat grain". The other metabolites and ethiozin were found to be stable in frozen storage for at least one year, but recoveries for DA at one year were marginally acceptable (≈60%).

It is not surprising that DK is stable in wheat grain but not wheat forage or straw. The wheat metabolism study has demonstrated that when metribuzin is applied to wheat forage or straw, much of the residue becomes irreversibly bound to the lignin. Significantly, metabolite DK is the only major triazinone metabolite which retains the reactive amino ($-NH_2$) group found in the parent. Because there is no substantial lignin fraction in wheat grain, such bonding could not occur. Given the structural similarities between the the two herbicides, it is surprising that ethiozin appears to show greater storage stability than does metribuzin.

There are several anomalies in the storage stability results for DK. For example, the percentages of ^{14}C-DK found on the TLC plates for wheat forage and beef kidney, as reported in Appendix XII of the report, are given in Table I.

Table I

Percent of ^{14}C-DK on TLC

Matrices	Sampling Interval					
	0-Day	30-Day	90-Day	270-Day	1-Year	2-Year
Beef Kidney	78.3	64.5	38.1	35.0	43.6	84.4
Wheat Forage	72.1	32.7	34.3	24.5	29.4	89.4

The percent of ^{14}C-DK present on the TLC plate is just one of several factors used to determine recovery. However, the fact that the 2-year values are significantly higher than even the 0-day values suggests that there may be a problem with the analytical method.

As noted, in our 10/27/89 memo we requested a storage stability study using corn. SENCOR® is registered only for preemergent use on field corn and is not registered for use on sweet corn. In view of the above data, we feel that a storage stability study on corn for preemergent uses would probably produce no useful information. At PHI's >100 days, levels of DK (and probably) parent would be very low. On the other hand we strongly concur with the Residue Chemistry Chapter of the Registration Standard, which stated that any additional data be generated from samples stored (frozen) **no longer than 2 weeks prior to analysis.** For storage periods longer than 2 weeks, accompanying storage stability data on parent, DA and DK must be submitted. DADK is stable under frozen storage and need not be tested.

Other Considerations

Our previous memo inadvertantly omitted an evaluation of Mobay's proposed tolerances for barley forage (2.0 ppm) and barley hay (7.0 ppm).

The Registration Standard Guidance Document, Table A, Footnote 25 states

> The available data are adequate to support tolerances on barley straw. Tolerances of 2 ppm for residues of metribuzin must be proposed for barley forage and straw. Alternatively, the present restriction against feeding or grazing barley prior to maturity may be amended to prohibit grazing or feeding treated barley, in any stage of maturity, to livestock. If tolerances are sought no additional data are required because data on wheat forage and data requested for wheat hay will be translated to barley forage and hay.

The current tolerance for barley straw is 1.0 ppm. The Registration Standard Residue Chemistry Chapter states that the "...available data support the established tolerance for metribuzin residues in or on barley straw...." The petitioner notes that there is a discrepancy between the Guidance Document and the Residue Chemistry Chapter and has not proposed to

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increase the tolerance for barley straw.

Since the Agency has stated that data on wheat forage and hay will be sufficient to support tolerances on barley forage and hay, Mobay has proposed tolerances of 2.0 ppm for metribuzin residues on barley forage and 7.0 ppm for metribuzin residues on barley hay. A tolerance of 2.0 ppm on wheat forage has already been established; the petitioner is proposing a tolerance of 7.0 ppm on wheat hay.

DEB Comment

Since the residue chemistry requirements outlined in the Guidance Document are based on the review given in the Residue Chemistry Chapter, we conclude that the Residue Chemistry Chapter is correct. A tolerance of 2.0 ppm for metribuzin residues in/on barley straw is not necessary.

In our previous memo, we agreed with Mobay's proposed tolerance of 7.0 ppm for metribuzin residues in/on wheat hay. Therefore, the proposed tolerance of 7.0 ppm for these residues in/on barley hay is appropriate. Since there is already a tolerance of 2.0 ppm for residues on wheat forage, a tolerance of 2.0 ppm for metribuzin residues on barley forage is appropriate.

cc: RF, SF, Circu., Metribuzin Reg. Std. File, ISB/PMSD(Eldredge), PP#8F3683/FAP#8H5563, Reviewer(MikeFlood), Stephanie Willett(DEB).

H7509C:DEB:Reviewer(MTF):CM#2:Rm810:557-4362:typist(mtf):11/17/89.
RDI:SectionHead:RSQuick:11/21/89:BranchChief:RDSchmitt:11/21/89.