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Date Out EAB: JUL 08 1985

TO: R. Taylor
Product Manager # 25
Registration Division
TS-767

FROM: Samuel M. Creeger, Chief 
Environmental Chemistry Review Section No. 1
Exposure Assessment Branch
Hazard Evaluation Division

Attached please find the environmental fate review of:

Reg./File No.: 1471-148

Chemical: Benefin and oryzalin

Type Product: Herbicide

Product Name: XL 2G (Balan XL ?)

Company Name: Elanco

Submission Purpose: Data review to fill EF data gaps

Action Code: 575

Date In: 5/6/85

EAB # 5586

Date Completed: JUL 08 1985

TAIS (Level II)

Days

62 ?

4

Deferrals To:

 Ecological Effects Branch

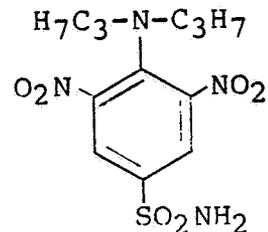
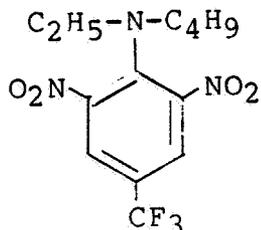
 Residue Chemistry Branch

 Toxicology Branch

1. CHEMICAL:

- o Product name: XL® 2G (? Balan XL)
- o Common name: Benefin Oryzalin
- o Chemical name: N-butyl-N-ethyl- α,α,α -trifluoro-2,6-dinitro-p-toluidine 3,5-dinitro-N⁴,N⁴-dipropyl sulfanilamide .

o Chemical structure:

2. TEST MATERIAL:

- o Pure (100 %) benefin for hydrolysis study;
- o Uniformly ring-labeled ¹⁴C-benefin (3.77 uCi/mg, 96.1 % radiopurity) for aerobic soil metabolism studies;
- o Uniformly ring-labeled ¹⁴C-oryzalin (16.7 uCi/mg, 98.0 % radiopurity) for aerobic soil metabolism studies.

3. STUDY/ACTION TYPE:

Data submission (EPA Acc. No. 257843) to fill environmental fate data gaps.

4. STUDY IDENTIFICATION:

- o Saunders, D. G., Smith, S. K. and Mosier, J. W., "Hydrolysis of the Herbicide Benefin in Aqueous Buffer Solution," EWD847, Lilly Research Laboratories, February 1985.
- o Berard, D. F., "Dissipation of ¹⁴C Benefin in Soils Maintained under Aerobic Conditions," ABC-0289, Lilly Research Laboratories, March 1985.
- o Berard, D. F., "Dissipation of ¹⁴C Oryzalin in Soils Maintained under Aerobic Conditions," ABC-0290, Lilly Research Laboratories, March 1985.

5. REVIEWED BY:

Soobok Hong
Chemist

Environmental Chemistry Review Section 1/EAB/HED

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7-8-85

6. APPROVED BY:

Samuel M. Creeger, Chief
Supervisory Chemist
Environmental Chemistry Review Section 1/EAB/HED

Samuel M. Creeger
JUL 08 1985

7. CONCLUSIONS:

- 7.1 Among the studies included in the present submission, only the hydrolysis study with benefin has been accepted. Deficiencies have been found in the aerobic soil metabolism studies with both benefin and oryzalin.
- 7.2 The following is the summary of environmental fate reviewed by EAB/EFB as of this review:

Benefin

- o Hydrolysis: Stable to hydrolysis under environmental conditions.

The hydrolysis data requirement has been satisfied.
- o Aerobic soil metabolism: Benefin metabolized in aerobic soil with a half-life range of 2.5-8.2 weeks depending on soil type. Soil binding was the major route of dissipation. Polar/nonpolar degradation products were minor. Production of volatile metabolites were evident, but identification and quantitation of them were not tried.

This data requirement has not been satisfied.
- o No other data requirements have been satisfied.

Oryzalin (Most of the summaries are taken from EAB review of 4/24/84.)

- o Hydrolysis: Stable to hydrolysis under environmental conditions.

The hydrolysis data requirement has been satisfied.
- o Aqueous photolysis: Appears to photodegrade in aqueous solution with a half-life of 4 days. However, the study is deficient in that material balance was not presented.

The data requirement has not been satisfied.
- o Soil photolysis: Photodegradation of the WP formulation on soil surface is inconclusive. (Note: 3/10/80 review mentions that a study was under way at the time to provide data on material balance. To date it has not been submitted.

The data requirement has not been satisfied.

- o Aerobic soil metabolism: Oryzalin is metabolized in aerobic soil with a half-life range of 1.6-5.7 weeks depending on soil type. Soil binding was the major route of dissipation. Polar/nonpolar degradation products were minor. Production of volatile metabolites were evident, but identification and quantitation of them were not tried.

This data requirement has not been satisfied.

- o Anaerobic soil metabolism: Oryzalin has an anaerobic soil half-life of 20-23 days. Degradation products include OR-2, OR-4, OR-13, and tentatively OR-15.

The data requirement has been satisfied.

- o Leaching: Oryzalin does not present a potential for leaching. However, it has a potential to build-up in soil as bound residues from yearly applications and runoff via erosion of soil particles. (Note: Some movement of residues from the 0-3 inch soil layer to the 6-12 inch layer was noted in some fields of "heavy" soils.) The company must address the question of whether use of oryzalin in tile-drained orchards will lead to oryzalin residues leaving the treated field via the subsurface drainage system.

The data requirement has been satisfied.

- o Field dissipation: Oryzalin has a half-life of 30-163 days depending on soil types under field conditions. A heavy clay soil resulted in longest persistence. The half-life of total (^{14}C) residue in the field is 58-77 weeks. Information on field degradation products not included in reviews.

The data requirement has not been satisfied.

- o Rotational crops: Oryzalin may have the potential to transfer to leafy green and root crops if crops are planted earlier than one year in soil treated with oryzalin. Small grain crops may be planted as rotational crops 4 months after application. Any residue taken up would be incorporated into natural plant constituents.

With a rotational crop restriction prohibiting the planting of leaf green and root crops earlier than one year after treatment with oryzalin, the data requirement has been satisfied.

- o Fish accumulation: Oryzalin has a potential to bioaccumulate in fish, but residues decline when fish are unexposed. Bioaccumulation factors for bluegill sunfish are 37-59X for edible tissue and 180-550X for viscera.

However, the data requirement has not been satisfied because no information was provided on the 38 % of the ^{14}C residues

unaccounted for in bluegill sunfish exposed to the 1.0 ppm concentration flow-through system.

8. RECOMMENDATIONS:

8.1 Benefin:

- o Only the hydrolysis data requirement has been satisfied for benefin.
- o All other requirements stated in the Guidelines need to be satisfied.

8.2 Oryzalin:

- o The following data requirements have been satisfied for oryzalin:
 - † Hydrolysis
 - † Rotational crops (with a one-year restriction)
 - † Anaerobic soil metabolism
 - † Leaching
- o The following data have been reviewed, but deficiencies were found:
 - † Aqueous/soil photolysis: Data on material balance. A previous review mentioned that a study was underway to resolve this deficiency. To date, it has not been submitted.
 - † Aerobic soil metabolism: Volatile degradation products (CO₂ or organic volatiles including parent compound) have not been trapped for identification and quantification.
 - † Field dissipation: Data on identity and rates of formation and decline of degradation products found in aerobic soil metabolism study.
 - † Fish accumulation: Information is needed on the 38 % of the ¹⁴C residues unaccounted for in bluegill sunfish exposed to the 1.0 ppm concentration flow-through system.
- o Although the leaching data requirement has been filled, we request the registrant to address the issue of whether use of oryzalin in tile-drained fields and orchards will lead to oryzalin residues leaving the treated field via the subsurface drainage system.

9. BACKGROUND:

A. Introduction

Elanco has submitted environmental fate studies on benefin and oryzalin, the active ingredients of XL® 2G herbicide. Although both compounds are registered, EAB files reveal that environmental fate data gaps exist for both compounds.

B. Directions for Use

EAB review of 2/2/84 provides the following:

Rates of application for preemergence control would be about 2 to 3 pounds ai per acre, applied in late winter or early spring. In some areas, a second application may be made at the same rates 8 to 10 weeks later. The product is applied by drop or rotary spreader. Two passes at half the recommended rate at right angles to each other are recommended for more even coverage.

The above directions for use are for BALAN® XL (1 % each of the ai's). The present submission is concerned with XL® 2G. The reviewer assumes that XL® 2G is identical with BALAN® XL.

10. DISCUSSION OF INDIVIDUAL STUDIES:

10.1 A. Study Identification

Saunders, D. G., Smith, S. K. and Mosier, J. W., "Hydrolysis of the Herbicide Benefin in Aqueous Buffer Solution," EWD8447, Lilly Research Laboratories, February 1985.

B. Materials and Methods

A laboratory hydrolysis study was conducted with chemically pure benefin (100 %) in buffer solutions (pH 5, 7 and 9) at 0.05 ug/ml under sterile conditions in the dark at 26°C.

The hydrolysis solutions were contained in 20-ml glass ampules. Twenty ml of the appropriate buffer were added to each ampule, the ampules (10 for each pH) were capped and autoclaved. For the fortification of the buffer solutions, a stock solution of benefin was prepared at 100 ug/ml in acetonitrile. Using a syringe, a 0.01 ml portion of acetonitrile solution was added to each ampule, and the neck of the ampule was immediately sealed in a flame. Five additional ampules at each pH were fortified with 0.01 ml acetonitrile only and served as controls.

Two fortified ampules and one control at each pH were analyzed at 0, 7, 15, 23, and 30 days. At each sampling period, two additional ampules at each pH were fortified

with 0.1 ug benefin and analyzed to determine the efficiency of the analytical method.

Determination of benefin in buffer solutions was done by GC after extracting the solution with dichloromethane (2X), evaporating to dryness and redissolving in toluene.

The average recoveries of benefin from the buffer solutions were ranged 87.8-91.2 %.

C. Reported Results

The results of the hydrolysis study are presented in Table II. No degradation of benefin was observed at any pH studied.

D. Study Author's Conclusion

These results indicate hydrolysis is not a mechanism of dissipation of benefin in the environment.

E. Reviewer's Discussion and Interpretation of Study Results

Benefin appears to be stable to hydrolysis under environmental conditions.

The hydrolysis data requirement for benefin has been satisfied.

10.2 A. Study Identification

Berard, D. F., "Dissipation of ^{14}C Benefin in Soils Maintained under Aerobic Conditions," ABC-0289, Lilly Research Laboratories, March 1985.

B. Materials and Methods

Uniformly ring-labeled ^{14}C -benefin (3.77 uCi/mg, radiopurity of 96.1 %) was incorporated into sieved (1.651 mm) sandy loam, silty loam and clay loam soils (see table 2 for soil characteristics) at a nominal concentration of 1 ppm with a 2.025 mg/ml methanol solution. The treated soils were well mixed, placed in loosely covered glass jars and maintained at 75 % of 0.33 bar moisture in the dark at 24°C.

Duplicate 25-g (wet weight) and one 10-g (wet weight) samples were removed 0, 1, 2, 4, 8, 12, 16 and 24 (except sandy loam soil) weeks after treatment. Total soil radioactivity was determined by combustion analysis. Duplicate 25-g soil samples were swirled in methanol and filtered. An aliquots of each filtrate was mixed with an equal volume of water and introduced onto a reverse-phase chromatography adsorbent. After collecting the aqueous methanol solution passing through the adsorbent, the nonpolar radioactivity was eluted with CH_2Cl_2 . Aliquots of the aqueous and CH_2Cl_2 eluents were radioassayed by LSC. Aliquots of the CH_2Cl_2

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eluent were also subjected to TLC (silica gel 60 F254, hexane:methanol=97:3, CCl₄:toluene= 80:20) with potential degradation products (table 1) for identification of metabolites.

C. Reported Results

The analysis of sandy loam, silty loam and clay loam soils treated with ¹⁴C benefin is shown in tables 3, 4 and 5, respectively.

During the 16-week sampling period, total radioactivity and ¹⁴C benefin in the sandy loam soil declined to 77.2 % and 5.5 % initial concentrations, respectively. In silty loam and clay loam soils, degradation was slower.

¹⁴C-Benefin degradation was also accompanied by an increase in soil-bound radioactivity. At the end of sampling period, 16 weeks for sandy loam soil and 24 weeks for silty loam and clay loam soils, soil bound radioactivity represented 59.7 % 66.1 % and 51.3 % of the initial radioactivity in the soils, respectively.

Radioactivity other than ¹⁴C-benefin having nonpolar characteristics accounted for 5-9 % of the initial radioactivity and consisted of several components, the most abundant of which represented 2.2 % of the initial ¹⁴C. Radioactivity cochromatographing with individual dealkylated and reduced reference compounds represented 1.0 % or less of the soil radioactivity (table 7). Polar degradation products represented an average of 7.0 % of the initial ¹⁴C.

The production of volatile degradation products was evident by declines in total soil radioactivity during the sampling periods. Losses of radioactivity ranged from 22.8 % in the sandy loam soil, where the ¹⁴C-benefin degradation was the highest, to 7.2 % in the clay loam soil.

The first-order half-lives of benefin in sandy loam, silty loam and clay loam soils were 2.5, 4.0 and 8.2 weeks, respectively.

D. Study Author's Conclusion

¹⁴C-Benefin degraded rapidly in coarse, medium, and fine textured soils maintained in the laboratory under conditions of constant temperature and moisture. While the majority of radioactivity present at the conclusion of the study was not extractable from the soil (soil-bound), low levels of polar and nonpolar degradation products were present. The dealkylated and reduced compounds identified in this study by cochromatography support the degradation pathway (figure 7) proposed for benefin and other dinitroaniline herbicides.

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E. Reviewer's Discussion and Interpretation of Study Results

Benefin appears to be degraded in aerobic soils with an estimated half-life range of 2.5-8.2 weeks depending on the soil type. Soil binding was the primary route of dissipation. Polar/nonpolar degradation products were minor.

However, this study cannot be acceptable because the volatile metabolites were not trapped; therefore, the identity and the quantity of the volatile compounds were not known. Assuming the unrecovered radioactivity was totally due to the loss via volatile compounds, 7.2-22.8 % of the original radioactivity was volatilized.

The nontrapped volatile compounds need to be identified and quantified.

10.3 A. Study Identification

Berard, D. F., "Dissipation of ^{14}C Oryzalin in Soils Maintained Under Aerobic Conditions," ABC-0290, Lilly Research Laboratories, March 1985.

B. Materials and Methods

Aerobic soil metabolism of ^{14}C -oryzalin (uniformly ring-labeled, 16.7 uCi/mg, 98.0 % radiopurity, diluted to 3.31 uCi/mg with technical grade oryzalin) was studied in sandy loam, silty loam and clay loam soils. The soils used in this study and methods were the same as in the benefin study (see section 10.2, above).

C. Reported Results

The analysis of sandy loam, silty loam and clay loam soils treated with ^{14}C -oryzalin is shown in tables 3, 4 and 5 respectively. During the 16-week sampling period, total radioactivity and ^{14}C -oryzalin declined to 75.1 % and 3.1 % of initial concentrations, respectively. In silty loam and clay loam soils, degradation was slower.

^{14}C -Oryzalin degradation was also accompanied by an increase in soil-bound radioactivity. At the end of sampling period, 16 weeks for sandy loam soil and 24 weeks for silty loam and clay loam soils, soil bound radioactivity represented 66.7 % 72.6 % and 66.8 % of the initial radioactivity in the soils, respectively.

Nonpolar degradation products accounted for 0.9-3.4 % of the initial radioactivity. Quantitative radiochemical determinations demonstrated that radioactivity cochromatographing with individual dealkylated and reduced reference compounds (table 1) represented 0.8 % or less of the soil radioactivity (table

7). Polar degradation products represented maximum concentrations of about 10 % of the initial radioactivity before declining to lower levels at the end of the sampling period.

The first-order half-lives of ^{14}C -oryzalin were calculated to be 1.6, 2.7 and 5.7 weeks in sandy loam, silty loam and clay loam soils, respectively.

D. Study Author's Conclusion

^{14}C -Oryzalin degraded rapidly in sandy loam, silty loam and clay loam soils maintained under laboratory conditions. Half-lives of oryzalin in these soils were 1.6, 2.7 and 5.7 weeks, respectively. The increase in soil-bound radioactivity and the presence of low level polar and nonpolar products, less than 10 % of initial radioactivity, were observed. The presence of low levels of dealkylated and reduced metabolites observed in this study supports the degradative pathway proposed for oryzalin and other dinitro-anilines (figure 7).

F. Reviewer's Discussion and Interpretation of Study Results

Oryzalin appears to degrade in aerobic soils with an estimated half-life range of 1.6-5.7 weeks depending on the soil type. Soil binding was the primary route of dissipation. Polar/nonpolar degradation products were minor.

However, this study cannot be acceptable because the volatile metabolites were not trapped; therefore, the identity and the quantity of the volatile compounds were not known. Assuming the unrecovered radioactivity was totally due to the loss via volatile compounds, 9.7-24.9 % of the original radioactivity was volatilized.

The nontrapped volatile compounds need to be identified and quantified.

11. ONE-LINER: A one-line for each compound has not been initiated.
12. CBI: No CBI is included in this review.

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