EEB BRANCH REVIEW

DATE: IN _____ OUT _____ IN 1/29/76 OUT 4/14/76 IN _____ OUT _____

FISH & WILDLIFE (ENVIRONMENTAL CHEMISTRY) EFFICACY

FILE OR REG. NO. 1471-35

PETITION OR EXP. PERMIT NO.

DATE DIV. RECEIVED

DATE OF SUBMISSION

DATE SUBMISSION ACCEPTED (3)(C)(1)(D) STATUS = 2C YES ?

TYPE PRODUCT(S): I, D,(H,)F, N, R, S

PRODUCT MGR. NO. 23 (Mountfort)

PRODUCT NAME(S) Treflan

COMPANY NAME Elanco Products

SUBMISSION PURPOSE New use pattern for control of Red Rice

CHEMICAL & FORMULATION Trifluralin (α,α,α-trifluoro-2,6-dinitro-N,N,-dipropyl-p-toluidine)

1 Introduction

1.1 Applicant has proposed an amendment to the registered use pattern for Trifluralin. He wishes to apply Trifluralin at twice the normal rate to control Red Rice (Oryza Satiwa) in soybeans. Use is requested only in the states of Arkansas, Louisiana, Mississippi, and Texas. Crop rotation with rice is proposed. This rate has been previously approved on soybeans, 7/9/75.

1.2 A data package consisting of 48 environmental chemistry studies has been submitted; while this data has not been previously reviewed, the majority of the studies date from the early 1960's and do not give enough supporting data (i.e., cultural practices, soil types, etc.) for an independent scientific judgement to be made. Consequently, it is not necessarily possible to draw general conclusions from this data submission.

1.3 Another name for this product is Treflan EC.

1.4 Treflan contains 1 lb. a.i./quart.

2.0 Directions for Use

Use in the states of Arkansas, Louisiana, Mississippi and Texas only.

Apply TREFLAN the first year anytime in the spring before planting at the following broadcast rates per acre:

Soil Texture	Pints Per Acre
Coarse soils	2
Medium soils	3
Fine soils	4
Coarse soils with 2 to 5% organic matter	3
Soils with 5.1 to 10% organic matter	4

Do not apply more than 4 pints per acre.

Apply TREFLAN the second year at the following normal label rates:

Soil Texture	Pints Per Acre
Coarse soils	1
Medium soils	1 1/2
Heavy soils	2
Coarse soils with 2 to 5% organic matter	1 1/2
Soils with 5.1 to 10% organic matter	2 to 2 1/2

If high amounts of organic matter (4 to 10%) and charcoal are present in the soil, apply TREFLAN the second year at the following rates:

Soil Texture	Pints Per Acre
Coarse soils	1 1/2
Medium soils	2 1/2
Fine soils	3

Incorporate TREFLAN thoroughly with a disc set to cut 4 to 6 inches deep or a field cultivator set to cut 3 to 4 inches deep.

This is a 2-year program over-all. Use the rates listed for first year application and plant soybeans. The second year, use the normal TREFLAN rate or the rate for charcoal soils and plant only those crops for which TREFLAN has been registered as a preplant treatment. Do not plant rice the second year. Rice may be planted the third year.

2.2 The remainder of the use directions are those on the approved label for TREFLAN.

3.0 Discussion of Data

3.1 Soil metabolism studies

3.1.1 ^{14}C Aerobic Study

(Kearney and Kaufmann - Degradation of Herbicides; Ref #1). This study is not primary data, rather it is a compendium of data referenced. A mixture of 85% trifluoromethyl label and 15% ring label ^{14}C-Trifluralin was applied to field soil.

The soil was extracted with aqueous methanol and assay done by LSC and combustion-LSC. The metabolites in extract were analyzed by TLC, GLC and GLC-Mass Spec.

Results of Aerobic Soil Study
% of applied ^{14}C

Months	Extractable Trifluralin	Total ^{14}C
2	52	80
4	33	78
6	28	75
10	23	70
20	5	58
28	2	50

Results:

Metabolites were present in only small amounts and did not build up. Main metabolites were mono and di-dealkylated Trifluralin and Benzimidazole compounds.

Conclusions:

1. Under aerobic conditions parent compound undergoes oxidative dealkylation, followed by a build up of bound residues.

2. Half life of parent was 2-4 months but half life of total ^{14}C was 28 months.

3. Bound residues comprised over 50% of applied ^{14}C after 2 months.

4. Based on other studies submitted, this reference is not germane.

3.1.2 Anaerobic Soil Metabolism (Ref #1, Kearney and Kaufmann).

Water was used to generate anaerobic conditions.

Results of Anaerobic Soil Study
% of Applied ^{14}C

Days	Parent	Extractable Degradation Products	Bound
2	90	10	5
6	10	20	30
10	5	40	40
14	3	50	50

Degradation products were mono and di-amine derivatives of Trifluralin.

The position of the ^{14}C label was not given.

Conclusions:

1. Parent compound is extremely rapidly degraded.

2. Confusion exists with regard to the degradation mechanism, though a microbial degradation appears to be favored.

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3. Route of degradation involves reduction of nitro groups to produce amino products which are further degraded to residues which become bound.

4. This study by itself is not germane based on other studies submitted.

3.1.3 Degradation of Trifluralin, Oryzalin and Isopropalin in Soil (Ref #2, Elanco).

Ring labelled Trifluralin was incorporated into 0-3" of a silty loam field soil plot at normal application rate. Soybeans were planted. Soil was extracted with methanol/water.

Analysis was by combustion-LSC, GLC, GLC-Mass Spec., and TLC.

Dissipation of Trifluralin in Soil

Months	Extractable Trifluralin	Total ^{14}C
2	30	75
4	15	70
10	12	65
16	10	50

No one degradation products ever constituted more than 4% of applied ^{14}C.

Degradation products consisted of various mono and di dealkylated, mono and di amino, and benzimidazole derivatives of Trifluralin.

Conclusions:

1. Parent compound has a half life of under 2 months; bound residues build very rapidly.

2. No major metabolites were found. Degradation involved dealkylation of propyl groups, reduction of nitro to amino groups and other changes in the side chains.

3. Bound residues are persistent, constituting from 40-55% of applied between 10-16 months.

4. Soil characteristics and rainfall data were not submitted.

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3.1.4 Determination of C-Nitroso and N-Nitroso Degradation Products in Field Soil Treated with ^{14}C-Trifluralin
(Ref. #3 - Elanco)

Ring labelled or mixed label (15% ring, 85% trifluoro methyl) Treflan was applied to field plots at 0.75-6.0 lb/A, and incorporated into 0-3" soil, 6-24-24 fertilizer was added at 500 lb/A and soybeans were planted.

The analytical method was methanol extraction, methylen chloride partition, TLC - co chromatography.

Conclusions

1. The compounds α,α,α-trifluoro-6-nitro-2-nitroso-p-toluidine and α,α,α-trifluoro-2,6-dinitro-N-nitroso-N-propyl-p-toluidine were not found to concentrations of .0005 ppm.

2. Soil and rainfall data were not given for this field test.

3.1.5 Persistence and Metabolism of Trifluralin in Soil
(Ref. #4 - USDA, Kearney, Plimmer, Wheeler, Kontson)

10 ppm ^{14}C (trifluoromethyl label) Trifluralin was incorporated into soil in a dark covered glass beaker.

At intervals soil was extracted with benzene/ethyl acetate followed by combustion. Extract was analyzed by TLC, LSC, and GLC - Mass Spec.

Soil Characteristics: Sand 38.4%; Silt 49.4%; Clay 12.2%; O.M. 1.5%; pH 5.3.

% of Applied ^{14}C

Months	Extractable	Parent Compound	Bound
3	77	72	14
5	54	-	24
7	44	41	25

Degradation products detected were mono and didealkylated and benzimidazole derivatives of Trifluralin.

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Conclusions

1. Half life of parent compound was about 6 months, much longer than in the field studies. Bound residues also did not build up as fast as in the field studies though the slower degradation/ dissipation in the lab has been noted by many authors.

2. Almost all of ^{14}C present was either parent or bound residues, with only minor amounts of metabolites being present.

3.4.6 Behavior and Persistence of Trifluralin in Soil
(Ref. #9, Horowitz, Hulin, and Blomenfeld, Weed Research, 14, 213 (1974))

Artificial soils were made by mixing sand with various proportions of clay, lime, or peat. Trifluralin was then applied at various rates.

Analysis was by bioassay.

Results

1. A strong correlation between organic matter and soil adsorption was found. Lime had no effect on adsorption.

2. The rate of dissipation as measured by bioassay was considerably faster at 40°C than at 10°C.

3.1.7 Degradation of Trifluralin under Laboratory Conditions and Soil Anaerobiosis
(Ref. #11, Parr and Smith, Soil Science. 115, 55 (1973))

Trifluralin was added to pH 6.0 silt loam which was or was not amended with alfalfa meal, at 5.0 ppm. Soils were incubated under aerobic and anaerobic (under nitrogen or under water) conditions. Anaerobic soils were non sterile, sterile (autoclaved or potassium azide) or sterile (autoclaved) followed by reinnoculation.

Respiratory CO_2 and volatiles were trapped.

Soil and water samples were sonified with hexane/acetone, and assayed for Trifluralin and its degradation intermediates by GLC with an electron capture detector.

Except where noted, these soil degradation experiments were run in the dark.

Degradation of Trifluralin in Soil

% of Applied Trifluralin Remaining

Conditions:	Days: 5	10	20
Anaerobic - Nitrogen - alfalfa meal	15	2	<1
Anaerobic - Nitrogen	90	68	68
Anaerobic - Flooded alfalfa meal	95	90	55
Anaerobic - Flooded	90	87	83
Aerobic	95	90	85
Autoclaved	100	99	96
KN_3 inhibited - alfalfa meal	100	90	78

Hexane solutions of Trifluralin (1.0 and 0.1 ppm), when exposed to laboratory light, underwent dealkylation of the propyl groups. At higher pesticide concentrations (200 ppm), there was relatively little decomposition in light or dark. When autoclaved soils were reinnoculated with microorganisms, degradation proceeded. Simularly KN_3 appeared to delay degradation by about 6 days.

Rate of volatilization was greater from aerobic than anaerobic (under nitrogen) soils.

Conclusions

1. No information was supplied defining soil characteristics.
2. Degradation under anaerobic conditions was due to microbial metabolism.
3. Aerobic metabolism and photodegradation resulted in sequential dealkylation, while anaerobic metabolism resulted in reduction of nitro groups.

3.1.8 Fate of Trifluralin in Soil and Plants
(Partial Ref. #16, Probst, Golab, Herberg, Holzer, Parka, Schans, Tepe, Agr. and Food Chem., 15592 (1967))

Trifluromethyl labelled or cold trifluralin was used. Application rate was 0.75 lb/A for field and aerobic greenhouse studies and 8.0 ppm for anaerobic studies.

The following is a compilation of 7 charts covering 5 different experiments reported in this article.

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Persistence of Trifluralin in Soil

% of Applied

Incubation Conditions	Soil Type	Compound Assayed	Analytical Method	Days 20	40	80	120	600
Field	Miami Silt Loam	Total ^{14}C	LSC	25% after 1 year				
Field	Miami Silt Loam	Extractable ^{14}C	LSC	75	30	20	18	16
Field	Miami Silt Loam	Trifluralin	LSC-TLC	60	25	15	12	10
Lab - aerobic with soybeans		Extractable ^{14}C	LSC	78	58	48	40	
Lab - aerobic without soybeans		Extractable ^{14}C	LSC	80	68	60	52	
Lab 0% Field Moisture Capacity		Trifluralin	glc	90	75	-	-	
50% Field Moisture Capacity		Trifluralin	glc	85	78	-	-	
100% Field Moisture Capacity		Trifluralin	glc	85	78	-	-	
200% Field Moisture Capacity		Trifluralin	glc	20	8	-	-	
Flooded Soil 38°F Sterile		Trifluralin	glc	95	-	-	-	
Flooded Soil 38°F Non-Sterile		Trifluralin	glc	70	-	-	-	
Flooded Soil 76%F Sterile		Trifluralin	glc	1	-	-	-	
Flooded Soil 76°F Non-Sterile		Trifluralin	glc	0	-	-	-	

		7 Days	14 Days
Flooded Soil	Trifluralin	80	30
" "	Known Metabolites	34	14
" "	Polar Unknowns (origin)	28	23
" "	Non Extractable	30	55

Persistance of Trifluralin in Soil

Incubation Conditions		Soil Type		Bioassay % Activity Days 30	90	150
lab	no plant	Brookston	^{14}C label	72	60	52
lab	Soybean	Silty clay loam	^{14}C label	60	48	40
lab	Autoclaved	"		100	100	98
lab	Nonautoclaved	"		100	100	90

Conclusions

1. On flooded soil, half life of Trifluralin was 10 days, while on moist soil it was well over 40 days.

2. On flooded soil at 76°F, trifluralin almost totally degraded by 20 days, under both sterile and non-sterile conditions.

3. Under aerobic conditions, half life of trifluralin in the lab was over 80 days, while in the field it was about 30 days.

4. 1 year after application of labelled Trifluralin to a field plot, 25% of applied was bound.

5. Analysis of metabolites shows that aerobic metabolism proceeds through dealkylation of the propyl side drains, while under anaerobic conditions reduction of the nitro groups is the first step. Metabolites are degraded very rapidly to polar unknowns and non extractable residues.

6. Soil characteristics and rainfall must be reported.

3.1.9 Trifluralin and Deiphenamid Disappearance in Soil
(Ref. #25, Exp #637-203, Eli Lilly)

A crabgrass bioassay study was used to assess herbicidial activity in the laboratory.

Three soil types were used: Brookston silty clay loam, Princeton fine sand, and Houghton muck. Samples of each soil were autoclaved.

Herbicide was applied at rates of 4 and 8 ppm to sterile and non-sterile soils. A 16 ppm rate was also applied to the muck.

Conclusions

1. Rate of trifluralin breakdown as measured by bioassay was greater on non-sterile than sterile soil.

2. Trifluralin disappearance on muck could not be properly evaluated. Percent inhibition varied from month to month by such significant factors that no trends could be noted. Other studies have shown that high organic matter concentrations effect trifluralin. This is probably the problem in the present study.

3. After 14 months there was a 50% growth reduction on the loam and sand samples.

4. Information on soil types and soil depths were not supplied.

3.1.10 Soil Degradation and Residue Detection Method (Ref. #40) Procedure 5800390 EXPT AAD-1011

Data for evaluating a GC method for detection and calebration of the residues of Trifluralin are presented. The procedure is designated as 5800390.

Exp't AAD-1115A, 1115

Procedure 5800390 was used in the three tests that follow.

Metabolite II α,α,α,trifluoro-2,6-dinitro-N-(N-propyl)-p-toluidine was found at rates of .07, and .11 ppm when 4 and 6 lb ai/acre trifluralin respectively was put on sandy loam soil and aged 56 days. The experiment was repeated with simular results.

Exp't AAD-1120

No metabolites were detected. Soil used was silt loam.

Exp't AAD-1125

No metabolites were detected. The soil was Houston Black clay.

Procedure 5800400

This procedure will detect diazotizable amines. It can be made fairly specific when used in conjunction with other procedures.

Exp't AAD-1117, 1117A

Procedure 5800400 was used to detect diazotizable amines in soil aged 86 days under field condition. Results vary fairly widely; however, at 4 lb ai/acre less than .1 ppm more metabolite was found in samples than in controls.

Procedure 5800410

A GC method for identifying metabolite in 3,5 dinitro-4-methoxy-benzotrifluoride is presented.

Exp't AAD-1119, 1119A

Procedure 5800410 was used to attempt to characterize metabolite IV residues. When sandy loam soil was treated and aged for 104 days with 4 lb ai/acre herbicide no detectible residues were found.

Exp't AAD-1045, 1046

Samples were hydrolyzed and then analyzed under 5800310. The procedure doesn't aid in metabolite detection efficiency.

Conclusion

1. These studies give no information on soil type, rainfall, and field cultural practices. It is therefore impossible to judge the applicability of these results.

3.1.11 Trifluralin Content of Soil
(Ref. #26, Exp't #AAD-1030, Lilly)

Procedure 5800360 for Trifluralin soil analysis was evaluated in this lab study on Brookston Silty Clay Loam at 0, 1/2, 1, 2, and 4 ppm.

Conclusions

1. Procedure appears to be reproduceable and detect 70 to 90% of the herbicide. Slight positive Triflan detection was noted with control samples. Applicant notes that GC results support contamination of the control.

3.1.12 Soil Degradation
(Ref. #37-39, Eli Lilly)

This is a laboratory study in which cotton was grown in soil treated with ^{14}C Treflan. The label was on a propyl group. Apparently application rates were .75 and 1.5 ppm.

Soil were shaken with Treflan solution to exchange 14C herbicide bound with non labeled pesticide. No other analysis of bound residue was offered.

	PPM Found	
	.75 ppm	1.5 ppm
0-2" soil depth	.45 ppm	1.13 ppm

Conclusions

1. It appears that the propyl groups were cleaned; labeled CO_2 was expired. Some of this was from soil metabolism.

2. Moss of the ^{14}C labeled compound recovered was in the form of Treflan and not a metabolite.

3. Data was for the most part presented as relative percent radioactivity; no information was given to relate it to ppm in soil.

4. No information was given or soil type, cultural practices, rainfall or time of soil sampling. Therefore no conclusions regarding persistance can be made.

3.2 Photodegradation Studies

3.2.1 The Photodecomposition of Trifluralin in Water (Ref. #27, Crosby, Leitis, Bull. Env. Cont. and Tox. 10, 237 (1973))

Conclusions

1. Trifluralin dissolved in aqueous methanol when exposed to natural sunlight, produced 6 products in 2 minutes and 25 products in less than 3 hours. Principal product under acidic conditions was 2 amino, 6 nitro aaa trifluoromethyl toluidine. Under basic conditions the principal product was 2-ethyl-7-nitro-5-trifluoromethyl benzimidazole. Simular results were found in water solution at about 1/10 of the above rate.

2. A soil was saturated with trifluralin, made into an aqueous suspension and irradiated. The photoproducts thus formed were the same as those from irradiated aqueous solutions above.

3. Analysis was by gc which was shown in ref. 21 to give misleading degradation products.

3.2.2 Ultraviolet Irradiation of Solutions of Trifluralin (Ref. #34, Experiment # AAD-1009)

A 20 mg/ml and a 50 mcg/ml solution of Treflan were irradiated with a mercury lamp (253.6, 366.3, 435.8 Nm). The course of the degradation of the herbicide was followed by GC and IR methods.

Results:

1. One of the principal reactions was loss of the propyl groups.

2. Degradation was first noted in the concentrated solution after 8 hours. After 14 days, only one product was found by gc.

In the dilute solution degradation was noted after 1 hour. The reaction was not followed to the reduction of all fragments to a single compound. Analysis of the products was attempted; but no positive identification was made.

3. All aromatic nitro compounds are probably eventually eliminated.

4. Possibly all aromatic compounds are eliminated.

5. The photoproducts are highly volatile.

3.2.3 Occurrence of Trifluralin and its Photoproducts in Air (Ref. #20, Soderquist, Crosby, Moilanen, Seiber, and Woodrow, J. Agr. Food Chem. 23, 304 (1975))

Trifluralin was exposed to simulated sunlight in a vapor phase photoreactor for 12 days. Analysis was by glc - mass spec.

Photolysis of trifluralin on coated dust by sunlamp was studied. Analysis was by glc.

Air above fields treated with trifluralin was analyzed by glc. Fields that had Treflan soil incorporated and surface application were compared.

Controls were run along with each experiment.

Results

1. Photolysis of vapor resulted in formation of various dinitrotoluidines and benzimidazoles, all of which were postulated to be eventually converted into one stable photoproduct - 2-ethyl-7-nitro-5-trifluoromethyl benzimidazole. A vapor phase photolysis pathway was proposed.

2. Almost all of the vapor above trifluralin treated fields was parent compound, with some dealkylated trifluralin, and only traces of benzimidazole being found. Most volatilization occurs in the field within the first 3 days. Atmospheric residue time for sampled air was quite short and thus didn't allow photodegradation.

3. Photodegradation on dust occurred at same rate as on soil surface.

4. Rain on the field plots greatly increases volatilization; this was more dramatic on surface treatment plots.

5. Field test data indicates that photolysis of Trefluralin occurs on the soil surface and is then followed by volatilization. This may be due to the prejudice of locating air samples close to ground level. As prevaously discussed this limits time for vapor phase photolysis.

6. Soil characteristics must be supplied.

3.2.4 Photodecomposition of Trifluralin
(Ref. #21, Leitis, Crosby, J. Agr. Food Chem., 22, 842 (1974).

Trifluralin in a photoreactor was exposed to simulated sunlight while dissolved in aqueous methanol, or water. Detection was by instrumental methods including MS., GCMS, NMR, and UV.

Conclusions

1. Photolysis proceeded very rapidly, to many photo labile products which were in turn rapidly photodegraded. Photolysis was faster in methanol solution than in water.

2. The principal product under acidic conditions was 2-amino-6-nitro-a,a,a trifluoro-p-toluidine. Under alkaline conditions 2-ethyl-7-nitro-5-trifluoromethylbenzimidazole represented about 80% of the photoproducts in 24 hrs.

3. A decomposition mechanism was presented; it involves oxidative dealkylation, nitro reduction, and cyclazation.

4. Reliance upon glc for identification of trifluralin residues is dangerous as it can introduce artifacts and obscure the major photolysis products.

3.3 Volatilization Studies

3.3.1 Volatility and Photodecomposition of Trifluralin, Benefin and Nitralin.
(Ref. #18, Parochetti, Hein. Weed Science, 21, 469 (1973))

Soil characteristics

	% Sand	% Silt	% Clay	% O.M.	pH	CEC
Lakeland Sand	89.2	4.8	6.0	0.5	6.2	2.9
Hagerstown Loam	23.2	44.8	32.0	2.5	6.8	14.7
Sharkey Clay	11.2	23.8	66.0	2.5	5.0	46.4

Results

1. Volatility of trifluralin increased significantly as moisture increased to field capacity; it continued to increase to soil saturation. Granular pesticide evaporated much slower than spray over the range of soil moisture.

2. At field capacity after 3 hrs 3 and 8% of applied Trifluralin granular and spray formulation was lost due to volatility at 30°C. Volatization rate is inversely proportional to CEC.

3. No photodegradation of trifluralin on 3 soil types resulted after 72 hours exposure to U.V. light as determined by bioassay in a study that was designed to have low volatility losses.

3.3.2 Stability of Trifluralin in Sunlight (Ref. #33 Eli Lilly)

Exp't GLP 2-55

Trifluralin was sprayed on moist soil in the lab at .25 and .5 lb a.i./acre. The pots were placed in the sun for 0, .5, 2, 4, 8, 24, 32, and 56 hrs. and then residual toxicity was monitored by bioassay.

Conclusions:

1. No difference in activity was noted between the 2 application rates.

2. Trifluralin is volatile from moist soils: after 56 hrs. residual activity was about 40%.

Exp't GLP 2-58

The above study was repeated except the soil was dry when exposed to light.

1. Essentially no difference in activity was found between the 2 application rates.

2. After 56 hours there was a 75% inhibition at .25 lb and a 94% inhibition at .5 lb a.i./acre.

Exp't GLP 2-23

Treflan was sprayed on soil at 0, .5, 1, 2 lb a.i./acre and then subjected to autoclaving for various lengths of time up to 8 hours. Herbicidal activity was monitored by bioassay.

Conclusion:

1. After 4 hours in an autoclave no biological activity remained at any application rate.

3.3.3 Factors Affecting Vapor Loss of Trifluralin (Ref #19 Spencer, and Cliath. J. Agr. Food Chem. 22, 987 (1974))

Conclusions:

1. Trifluralin vaporized more rapidly when surface applied than when incorporated.

2. Application to dry soil resulted in essentially no volatilization.

3. Vapor density increased with soil moisture.

4. Vapor density was inversely related to soil organic matter content.

5. Other soil characteristics were tabulated. No significant correlation with evaporation was noted.

This was a lab study.

3.3.4 Trifluralin Loss Due to Volatility (Ref. #31, Lilly)

Exp't GLP 3-27

Trifluralin was sprayed on a soil surface. This container of soil was placed on top of a larger second container of soil that was planted with millet. The entire apparatus was sealed in a plastic tent for 7 days; the tent was then removed and the millet grown for 21 days. During the time the tent was installed, temperature and water vapor were not controlled and they both reached fairly high levels.

Conclusions:

1. Trifluralin caused an 88% inhibition of millet at .5 lb application rate and a 100% inhibition at 1, 2, and 4 lb a.i./acre.

2. Clearly trifluralin is rapidly evaporated from soil surfaces.

Exp't GLP 3-33

The procedure described above was used, except 20% WP and technical Treflan in acetone was sprayed at .5 lb a.i./acre.

Conclusion:

1. The wettable powder appeared to have a higher volatility and also greater residual activity based on bioassay.

Exp't GLP 3-57

The procedure described in GLP 3-33 was used, except the tents were removed after 3 days.

Conclusion:

1. The technical herbicide appeared to have greater volatility and residual activity based on bioassay.

2. Note that this is exactly opposite of the results in GLP 3-33.

3.3.5 Soil Adsorption and Volatility of Dinitroaniline Herbicides (Ref #17 Harvey, Weed Science 22, 120 (1974))

1. Trifluralin is readily absorbed by plano silt loam (sand 6%, silt 71%, clay 23%, O.M 4.0, pH 6.3, CEC 20). It is bound with a ΔH° absorption of about -12.2 Kcal/mole.

3.3.6 Evaporation Rate of Trifluralin (Ref #32 - Eli Lilly)

Weights of Treflan were put in planchets and in planchets plus brown sand. After 24 hours, weight loss was monitored.

Substrate	weight Treflan (mg)	W. loss rate mg/day/cm^2	% loss/ day
much sand	72.3	.0483	.07%
little sand	78.9	.0189	.02%
no sand	65.0	.0215	.03%

study was for 30 days at 25°C.

3.4 Soil mobility, diffusion and adsorption

3.4.1 Pesticide Mobility in Soils - Application of Soil TLC (Ref. #14, Helling Soil Sci. Soc. Amer. Proc. 35, 737 (1971))

1. Trifluralin falls into Helling and Turners' mobility class I on Hagerstown silty clay loam. This is a class of immobile pesticides.

2. Trifluralin was the only one out of 6 pesticides applied to a 500 micron TLC plate that did not leach at all.

3.4.2 Partition between Water and Mud (Reference #44)

Treflan E.C. was added at 1.0 lb/A to pools containing 5" mud and 2" water. Pools were stirred heavily or not stirred at all. Water and mud was analyzed.

Conclusions:

1. After 7 and 14 days Trifluralin had partitioned completely into the mud. After 14 days concentration in mud was about 1 ppm.

2. Information is not given on soil type used, control of volatilization, photodegradation or hydrolysis.

3. This was a cold study, we need to know the limits of analytical sensitivity for detection of Treflan in water.

3.4.3 Mechanism of Trefluralin Diffusion in Silt Loam Soil (Ref # 12 Bode, Day, Gebhardt, Goering, Weed Science 21, 480 (1973))

Diffusion of radiolabelled Trifluralin (85% $^{14}CF_3$, 15% ring labeled) through Mexico silt loam was measured in diffusion cells under laboratory conditions. Soil characteristics were silt 75%, clay 22%, O.M. 2.5%, pH 5.6.

Results:

1. Ficks second law with a constant diffusion coefficient adequately describes trifluralin diffusion regardless of time or concentration.

3.4.4 Leaching and Decomposition Studies with Pre-emergent Herbicides (Ref. #35, 36 Eli Lilly)

Exp't G35-213

Trifluralin was applied in the lab to Princeton fine sand, Brookston silty clay loam and Houghton muck at 2 and 4 lb. a.i./acre. After waiting 4 hours, 2, 4, 6, 8, and 10 inches of water was passed through the soil. Remaining herbicidal activity on the soil surface was evaluated by bioassay.

Conclusions:

1. Little leaching takes place under any conditions apparently.

2. Bioassay is not a suitable technique to evaluate leaching.

3. Soil characteristics are not given

Exp't G35-217, GLP 2-17

Princeton fine sand and Brookston silty clay loam was put into a segmented leaching apparatus. Herbicide was applied at 4 lb/acre and allowed to age for 4 hours. Ten inches of water was then run through the leaching apparatus, and the segments assessed for herbicide content by bioassay.

Conclusions

1. Using this detection method, Treflan is shown to leach 2-4" on sand.

3.4.5 Trifluralin Interactions with Soil Constituents (Ref #15 Hollist, Foy Weed Science 19, 11(1971))

1. An ion exchange capacity was a better parameter than cation exchange capacity, surface area, and adsorption from solution for determination of phytotoxicity.

   The effectiveness of organic matter in reducing phytotoxicity may be related to high surface area and exchange capacity.

   This was a lab study done in artificial soils.

3.4.6 Prediction of Trifluralin Diffusion Coefficients (Ref #13 - Bode, Day, Gebhardt, Goering Weed Science 21, 485 (1973))

Diffusion is low in air dry soils for all temperatures 4.4 to 49°C It increases to a maximum when the soil has between 8-15% w/w soil moisture and then decreases as moisture content increases. Soils and experimental treatments used are described in 3.4.3

Conclusions:

1. Vapor diffusion is the major component of total diffusion.

2. Trifluralin is strongly absorbed at low moisture contents.

3.4.7 Movement and Persistence of Bensulide and Trifluralin in Irrigated Soil (Ref. #10, Menges, Tamez, Weed Science 22, 67(1974))

Trifluralin was applied in 1969 and 1971 to sandy loam soil and incorporated at a depth of 1" and 3". Application rate was 1 lb a.i./acre. The soil content was sand 75%, clay 16%, silt 9%, O.M. .8%, pH 8.1. Pesticide content of the soil was monitored by bioassay.

Conclusions:

1. Trifluralin increases in persistence as the depth of incorporation increases.

3.5 Field Persistence

3.5.1 Trifluralin Dissipation in Soil Following Repeated Annual Applications (Ref #6 O.C. Burnside, Weed Science, 22, 374(1974))

Trifluralin was incorporated for 1 to 3 years at rates of 0, .5, 1, and 2 lb a.i./acre to Sharpsburg silty clay loam (Lincoln, Nebraska): sand 9%, silt 45%, clay 46%, O.M. 2.8%, pH 5.8, and CEC 27.

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Rainfall was 30.7, 28.0, 31.9, 35.0 inches 1969 to 1972 respectively. A phytotoxicity study, as shown below, indicated the buildup of toxic material in the soil for 1 to 2 years. Fields were fall plowed, and a cover crop of soybeans was planted.

Pesticide Application Rate lbs a.i./acre	Years Applied	Millet Yield lbs/acre		Oat Grain yield
		1970	1971	1972
0	1969	902	580	2357
	1969-70	884	857	2420
	1969-71	804	723	2268
.50	1969	723	643	2250
	1969-70	482	821	2392
	1969-71	563	482	2250
1.00	1969	893	757	2411
	1969-70	438	973	2277
	1969-71	348	36 580	2205 2402
2.00	1969-70 1969	821 80	616	2330
	1969-71	98	0	1339

However, as shown in the following data no build up of pesticide in the soil was noted.

Applied (years)	Trifluralin Rate	Trifluralin conc extracted from the soil 0-10 cm	10-20 cm
		1972 lb a.i./acre	
Untreated check		0	0
1969	.5	0	0
	1.00	0	0
	2.0	<0.01	<0.01
1969-70	.5	0	0
	1.0	0.01	0.01
	2.0	0.05	0.05
1969-71	.5	<0.01	<0.01
	1.0	0.05	0.09
	2.0	0.20	0.13

Conclusion:

1. As demonstrated from phytotoxicity, Trifluralin remains effective in the soil for 1 to 2 growing seasons. The effective agent is not monitored by Trifluralin analysis which shows little Trifluralin concentration in the soil after 1 season.

3.5.2 Soil Persistant of Trifluralin, Benefin, And Nitralin (Ref #7, Miller, Keeley, Carter, and Thullen Weed Science 23,211 (1975))

Trifluralin was applied, to Hesperia fine sandy loam (11% clay, 19% silt, 70% sand, .3% O.M.) at rates of .75 lbs a.i./acre for 5 consecutive years, as a PPI treatment to cotton. Rainfall was as follows 4.9, 6.5, 8.0, 5.8, and 5.5 "1966-70; it was confined mostly to November through February. Detection of herbicide was by GC with an electron capture detector.

Herbicide	Annual rate (lb/acre)	Time[b]	Residue in depth increment-(cm) 0-15 (ppmw)	15-30 (ppmw)	30-45 (ppmw)	45-120 (ppmw)
Trifluralin	1.5	1967	0.40	0.09	T	ND
		1968	0.20	0.06	T	ND
		1969	0.29	0.05	T	ND
		1970	0.28	0.06	T	ND
		+15 mo.	0.11	0.10	ND	ND
		+30 mo.	0.02	0.02	ND	ND

Conclusions:

1. Pesticide does not leach under field conditions.
2. Herbicide treatment did not appear to effect total cotton produced.
3. Bioassay with mullet indicated some pesticide residue.
4. No pesticide accumulation over the years was noted.
5. After 15 months final pesticide concentration in the soil reduced grain sorghum yeilds by 46%. There was no effective on sorghum growth after 30 months.

3.5.3 Nitralin and Trifluralin Persistence in Soil (Ref #8, K.E. Savage, Weed Science 21, 285 (1973))

1. In 250 fields which had a previous history of Trifluralin use, the average Trifluralin residue was 0.06 ppm. All soils were from Mississippi; average soil characteristics were reported.
2. Field soils were treated with 1.68 kg/ha for 5 years. GLC assay of soils showed residue at less than 0.1 ppm.
3. Autoclaving of Trifluralin treated soil had no influence on the rate of degradation in a lab study (glc assay).
4. Trifluralin was added to a fine sandy loam. Soil was pH 6.8 or adjusted to pH 4.8. The change in pH had no effect on the rate of Trifluralin dissipation as shown by glc assay.

Conclusion:

1. Extractable residues of Trifluralin did not build up after repeated applications at twice recommended dosage and frequency.

3.5.4 The disappearance of Trifluralin from field soil (Ref #5 S.S. Parka and J.B. Tebe Weed Science 17, 119(1969))

Soil treated with ~~Triforine~~ TREFLAN in the field from 107 locations about the country was tested for residues after 1 to 4 years of consecutive pesticide application. Application rates and data are summarized below. Samples were collected at the end of the growing season; five to seven months after pesticide application.

Herbicide detection was by GC using an electron capture detector.

Location	Soil type	Years of application	Total applied (lb/A)	Trifluralin remaining PPM
Western U.S.				
Arizona				
Welton	SaL	2	1.80	0.03
		3	2.80	0.03
Phoenix	Sal[b]	6	6.00	0.21
		6	24.00	0.98
Phoenix	SaCL[b]	1	0.75	0.06
		3	3.00	0.08
Phoenix	SCL	1	0.75	0.01
		2	2.00	0.05
Queen Creek . . .	SL	3	2.75	0.05
Yuma	CL	1	1.00	0.05
California				
Kingsbury	SaL	1	0.75	0.03
McFarland	SaL	1	0.75	0.04
		2	1.50	0.06
		3	2.25	0.07
McFarland	SaL	1	0.75	0.10
		2	1.50	0.08
		3	2.25	0.08
		3	2.25	0.08
		4	3.00	0.09

[b] Sampled to a depth of 0 to 3 inches.

Location	Soil type	Years of application	Total applied (lb/A)	Trifluralin remaining (PPM)
McFarland	SaL	3	2.75	0.19
		4	3.75	0.28
		4	4.75	0.28
Readley	SaL	2	1.50	0.09
Idaho				
Filer	SL	1	0.63	0.03
		1[c]	1.00	0.01
Nampa	SL	1	0.63	0.07
		1[c]	1.00	0.01
Utah				
Delta	CL	1	1.00	0.11
Washington				
Quincy	SaL	1	0.75	0.11
		2	1.50	0.26
		2[d]	1.50	0.14
Quincy	SL	1	0.75	0.10
Touchet	SaL	2	1.50	0.16
Central U.S.				
Colorado				
Erie	CL	1	0.75	0.03
		2	1.50	0.03
Kansas				
Barnes	CL	1	0.75	0.03
Nebraska				
Alliance	FSaL	1	1.00	0.01
Oklahoma				
Hinton	SaL	1	0.60	0.05
		2	1.20	0.04
		3	1.50	0.02
		4	2.70	0.09

[c]Application of trifluralin was made two crop seasons prior to sampling.

[d]Trifluralin was not applied to the field between the first and third crop seasons.

Location	Soil type	Years of application	Total applied (lb/A)	Trifluralin remaining (PPM)
Texas				
Donna	SaL	1	0.60	0.02
		2	2.00	0.04
LeFeria	SaL	3	3.00	0.03
Monday	SaL	1	0.50	LT0.01[b]
		2	1.00	0.02
McAllen	SaL	1	0.75	0.01
		2[c]	1.60	0.03
		3[c]	3.00	LT0.01[b]
McAllen	C	4	4.00	0.05
Edmondson	SaCL	1	0.75	0.03
		2	1.50	0.05
Edmondson	CL	3	2.34	0.13
		4	3.09	0.07
Fabens	SaCL	1	0.75	0.07
		2	1.50	0.10
		3	2.55	0.12
		4	3.25	0.18
Shallowater	SaCL	1	0.50	0.02
		2	1.00	0.03
		3	1.45	0.04
Eastern U.S.				
Arkansas				
Little Rock	SaL	1	0.75	0.02
		2	1.50	0.01
		3	2.25	0.06
		4	3.00	0.04
Mississippi				
Nettleton	SaL	1[b]	0.75	0.07
		2	1.43	0.11
		3	2.43	0.04

[b]Sampled to a depth of 0 to 3 inches.

[c]Application of Trifluralin was made two crop seasons prior to sampling.

Location	Soil type	Years of application	Total applied (lb/A)	Trifluralin remaining (PPM)
Tennessee				
Jackson	SaCL	1[b]	1.00	LT0.01[c]
		2[b]	2.00	LT0.01[c]
		3	3.00	0.03
		1[b]	2.50	0.01
		2[b]	5.00	0.02
		3	7.50	0.06
		1[b]	5.00	LT0.01[c]
		2[b]	10.00	0.06
		3	15.00	0.17
Mississippi				
Sidon	SL	3	2.50	0.07
Greenwood	SL	2	1.50	0.04
Holly Grove	SCL	1	1.00	0.09
Georgia				
Blakely	SaL	1	1.00	0.07
		2	2.00	0.07
		2[d]	2.00	0.10
		2	3.00	0.11
Blakely	CL	1	1.00	0.07
		2	2.00	0.10
		3	3.00	0.10
		4	3.20	0.07
Midville	SaL	1	0.75	0.07
		2	1.75	0.06
		3	2.00	0.14
		4	2.75	0.13
South Carolina				
Montmorenci	SaL	1	0.05	0.12
		2	1.25	0.06
		3	1.88	0.06

[b] Sampled to a depth of 0 to 3 inches.

[c] Application of Trifluralin was made two crop seasons prior to sampling.

[d] Trifluralin was not applied to the field between the first and third drop seasons.

Location	Soil type	Years of application	Total applied (lb/A)	Trifluralin remaining PPM
North Carolina				
Jackson	SL	1	0.75	0.06
		2	1.75	0.07
		3	2.75	0.02
Delaware				
Georgetown	SaL	2	1.25	0.10
Illinois				
Braceville	L	1	0.75	0.11
		1	0.75	0.23
New York				
Waterville	SL	1	1.00	0.06
Indiana				
Muncie	CL	1	1.20	0.07
		2	2.20	0.03
		3	3.20	0.06
Iowa				
Des Moines	SCL	1	1.00	0.10
		2	2.00	0.08

Conclusions:

1. Trifluralin levels do not build up, or build up very slowly in soil with use over many seasons.

2. No attempt was made to characterize metabolites.

3. Cultural practices, rainfall and soil characterizations are not submitted.

4. It should be noted that the analytical procedure used in the study appears to find low residues.

3.5.5 Trifluralin content of soil (Ref #27, 28, 29, 30 - Eli Lilly)

Experiment's AAD-1031, 1033, 1035, 1037 respectively

Trifluralin was applied to field plots at various rates and incorporated into 2 OR 3". Soil was analyzed by glc at one time interval after application for trifluralin and its metabolites using procedure 3800360.

Trifluralin and Metabolites in Soil

Soil; other studies	ppm applied	days	% of Applied Remaining	
cited using this soil	.75	110	37	
Sandy Loam	1.5	110	51	
AAD-1110,1114	2.9	110	39	
			0-3"	3-6"
Sandy Loam	4	60	11.5	67
AAD-1115,1119	5.8	60	19.8	.5
			0-8"	
Silt Loam	1	420*	< 0.05	
AAD-1120,1124	4	420	< 0.05	
			0-2"	
Clay	1.45	120	2	
AAD-1125,1129	2.9	120	2	

*A crop was planted in the soil and after harvest the soils was plowed to 8"

Conclusions

1. Herbicide does not leach; very little was found below 3".
2. This was not a hot study; no data was supplied on rainfall, cultural practices, or soil type.

3.5.6 Ref. 41

Experiment C3-1

Trifluralin was applied at rates to 10 lb. a.i./acre to rye. Persistence by bioassay showed no active residues 405 days after herbicide application. After 92 days only slight residues were found, and these were entirely in the 0-2" region.

Experiment MI-27

Previously reviewed 4/7/75 and accepted. Note that I believe there is an error in the previous review; data shown is for 25 lb a.i./acre rate, not 1.25.

Experiment GLP 2-62

Trifluralin was applied. Persistence was evaluated after 92 days by crabgrass bioassay. 11.65 inches of rain fell.

Conclusions

1. Bioassay yields little information with regard to leaching. The study is not germane based on other studies submitted.

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3.6 Field Leaching

3.6.1 Movement and Persistence of Bensulide and Trifluralin in Irrigated Soil (Reference #10 Weed Science)

Trifluralin was incorporated to a depth of 2.5 or 7.5 cm in fields planted to carrots for 3 consecutive years at 1.0 lb/acre.

Assay was by GLC and bioassay.

Soil Characteristics: Sand 75%; Silt 9%; Clay 16%; O.M. 0.8%; pH 8.1

Rainfall, evaporation and air temperature data was supplied.

Results:

1. Trifluralin residues were only found at the depth of incoporation.
2. No residue was detected after 12 months; a residue was detected after 6 months. Soil was disked before sampling.
3. Trifluralin dissipated much more quickly when soil was tilled.

Conclusions:

1. Trifluralin did not leach over a 6 month period under field conditions in a light soil; in fact, vaporization tended to increase the herbicide concentration near the soil surface even when it was incorporated at 3 inches.

3.7 Field Runoff Study (Ref. #42 - Exp. # C4-76)

Treflan was soil incorporated surrounding a polyethylene pool at 1 lb ai/A. No pesticide was applied within 18" of the pool. Polyethylene film was spread under the soil to the pool edge (2" deep for 10"). Silty clay loam soil was used. The pool was at the bottom of a hole developed by a 5 to 8° slope. Artificial rainfall was applied in increments, totaling 10", at 0.5"/hr. Three inches were applied and then a 16 hr. wait before water was applied, etc.

Results:

1. No detectable residues of Trifluralin were found in the water.
2. Soil sediment in pool contained 5.5 ppb Treflan.
3. These results are meaningless. The polyethylene was spread for a 10" region about the pool, but no pesticides were put down within 18" of the pool. Thus any pesticide migration besides runoff, couldn't enter the pool since the plastic lever and pool itself would prohibit entry. Pesticides were incorporated to 3" but the polyethylene was only buried 2".

3.8 Plant Metabolism

3.8.1 Fate of Trifluralin in Soil and Plants (Partial Ref. #16 - Agricultural and Food Chemistry)

Soybeans and cotton were grown in soil treated with trifluoromethyl or n-propyl labelled Trifluralin. Carrots were grown in soil treated with trifluormethyl labelled Trifluralin.

Analysis involved hydrolysis, TLC and glc.

Results

1. Radioactivity in cotton and soybeans for both labels was distributed in lipids, glycosides, hydrolysis products, protein and cellular fractions.

2. Hydrolysis of glycoside fractions revealed no trifluralin or major degradation products.

3. 97% of ^{14}C in carrots was extractable, with 93% partitioning into hexane. 84% of the radioactivity in the hexane was trifluralin and 4.3% was mono-de-alkylated trifluralin. Total ^{14}C in carrots ranged from .49 to .86 ppm

Conclusions

1. Trifluralin and its metabolites were not found as such or as glycosidic conjugates in cotton and soybeans. The propyl and trifluoromethyl side chains were probably metabolized off and incorporated into the cellular matter.

2. Trifluralin is absorbed and remains predominantly as extractable parent compound by carrots.

3. Treflan residues occur primarily on the peel of root crops.

3.9 Fate of Trifluralin in an Aquatic Environment

3.9.1 Accumulation of Six Dinitroaniline Herbicides on an Aquatic Microecosystem (Ref #45)

1 ppm ^{14}C-Trifluralin was adsorbed to soil in an aquarium in a greenhouse which was subsequently flooded with water. Organisms were added immediately, fish were added at day 30.

All organisms were harvested and radioassayed 33 days after initiation of experiment. Fish and water were also analyzed by TLC. Trifluralin concentration in water was about 5 ppb.

^{14}C residues in a model ecosystem
ppm as Trifluralin

	Water	Algae	Snails	Daphnids	Fish
Fresh wt.	0.007	2.07	3.0	.66	.24
Dry wt.	-	6.03	10.87	4.36	.97

TLC analysis of fish and water showed no trifluralin and mostly polar compounds.

Sealed quartz bottles of Trifluralin placed in aquarium at start of experiment, showed 90% degradation in 3 days. They, along with the above study were exposed to normal sunlight.

Conclusions

1. Trifluralin was rapidly photodegraded.

2. Bioaccumulation ratio ranged from 23x to 500x on all test organisms.

3. The study is not sufficient to determine accumulation.

3.9.2 The Fate of Select Pesticides in the Aquatic Environment (Ref 46 Samborn WSEPA - 660/3-74-025 Dec. 1974)

^{14}C Treflan was incorporated in sand at 1 lb a.i./acre in a model ecosystem; soybeans were grown. Sorghum was also treated with the pesticide. In the sorghum experiment caterpillars were added to disperse trifluralin into the food chain.

In the sorghum study, concentration of pesticide and metabolites reached .0388 ppm; whereas in the sand study it had a maximum of .00684.

The following bioaccumulation figures were presented:

based on Treflan

	sand treatment	sorghum treatment
fish	4212	926
snail	147201	17894

based on total ^{14}C

fish	210	46
snail	4250	340

Conclusions

1. Trifluralin will kill algae.

2. Once in soil little trifluralin is released to the aquatic system. However pesticide in or on plants easily enters the ecosystem through caterpillars.

3. Trifluralin bioaccumulates quite significantly in fish, snails and other members of the aquatic ecosystem.

3.9.3 Eli Lilly Fish Study (Ref. 43)

This is a fish toxicity study; it is not environmental chemistry data.

3.9.4 Exposure of Fish to ^{14}C Trifluralin: Accumulation, Distribution and Elimination of Residues (Ref. 47 Bionomics)

100 bluegill sunfish were exposed for 35 days to nominal 20 ppb ring labelled Trifluralin in a continuous flow dilution apparatus. Fish remaining were then placed in fresh water for 14 days. The mean measured concentration of herbicide was 7.87 ppb over the test period.

Analysis of fish tissue was by combustion-LSC, of water was by LSC.

Mean ^{14}C Residues in Fish and Water
ppb as Trifluralin

Day	Water	Edible Fish	Edible Fish Bioconcentration Factor	Nonedible Fish Bioconcentration Factor
1	4.29	5,500	1,280	-
7	9.98	12,000	1,200	10,000
14	10.10	7,390	730	-
21	6.27	6,910	1,102	-
28	11.27	8,060	715	-
35	8.74	7,930	907	-
Withdrawal				
1		6,290		
3		4,510		
7		790		
10		700		
14		750		

Partition of Residues in 35 day edible tissue

Hexane	58%
Methanol	4%
Non-Extractable	38%

32

Conclusions

1. Trifluralin bioconcentrated in the edible portions of fish to over 1200x by 7 days, but the residue levels declined thereafter.

2. After 7 days exposure to pesticide free water, 90% of the ^{14}C in the edible tissues was lost. However at the end of the study the herbicide concentration appeared to have leveled off at .75 ppm.

3. 58% of the residue in the edible tissues was hexane extractable and 4% was methanol extractable. The remainder was non-extractable.

4. Residues in edible tissue were not identified nor were nonedible tissue residues monitored as are presently required. This study was submitted in 1973 and never reviewed. In any case, the company has agreed to submit a chronic fish study in order to assess the hazard. This will remedy any problem areas remaining in the above study.

3.10 Effect of Microbes on Trifluralin

3.10.1 Identification of Trifluralin Metabolites from Rumen Microbial Cultures. Effect of Trifluralin on Bacteria and Protozoa (Ref. #23, William, Feil, J. Agr. Food Chem. 19, 1198(1971))

Studies used ^{14}C ring and side chain labeled herbicide. Identification was by TLC, Mass spec, I.R. and associated analytic techniques.

Conclusions

1. Rumen ciliated protozoa and bacteria tolerate relatively high concentrations of trifluralin.

2. Of 12 characterized rumen bacterial strains, only 2 degraded Treflan, no loss of methyl group or ring cleavage was found.

3.11 Animal Metabolism Studies

3.11.1 Fate of Carbon-14 Trifluralin in Artificial Rumen Fluid and in Ruminant Animals (Ref. #24, Golab, Herberg, Day, Raun, Holzer, Probst, Agr. and Food Chem. 17, 576 (1969))

Trifluoro labeled Treflan was used in the artifical rumen studies and a mixture of ring and trifluoro substituted herbicide was used in the other study.

Artificial rumen consisted of 30 minute old rumen fluid and artificial saliva. Herbicide was adsorbed in the cellulose of the saliva.

Analysis was by TLC and radiography.

In the animal study a lactating holstein cow was fed trifluralin incorporated alfalfa at 1 and 1000 ppm. Goats were used in the metabolism study.

Conclusions:

1. Treflan was degraded in about 11 hours to non-ethyl acetate extractables in rumen fluid. No 14C CO_2 or CH_4 was detected.
2. In ruminant goats, 9% of the ingested radioactivity from ^{14}C Treflan was recovered within 6 days (17.8 urine, 81.2% feces) as non identified polar compounds primarily.
3. No radioactive was recovered from milk or blood.
4. None of the recovered radioactivity was in the form of Trifluralin. The excreted products were primarily non-identified polar substances.
5. An analysis of rumen fluid extracts was performed to determine the metabolites and a metabolic pathway was proposed. Principle degradation is reduction of NO_2 groups.
6. Analysis of cow tissue showed .09 ppm herbicide and metabolites in the fat. No traces were found elsewhere. Analysis of goat tissue showed no evidence of residues. Concentrations in the blood were 2 ppb.

3.12 Effects of Pesticide on Microorganisms

3.12.1 Bacterial, Fungal, and Actinomycete Populations in Soils Receiving Repeated applications of 2,4-D and Trifluralin (Ref. #48, Breazeale, Camper, Applied Microbiology 19, 379(1970))

Soil samples were taken from plots that received repeated applications of Treflan in sandy loam soil (1 lb. a.i./acre for 5 consecutive years). They were tested in specific media for the above referenced organisms.

Treatment	Soil pH	Organisms/g of soil		
		Actinomycetes	Bacteria	Fungi
Control	6.3	24.50×10^4	83.45×10^4	12.02×10^4
Trifluralin	6.0	46.20×10^4	41.49×10^4	2.27×10^4

Conclusions

1. Actinomycete count was higher in the trifluralin treated soil than in the control. Bacterial and fungal counts were lower.

3.12 Degradation products

	Name	Found
a)	Trifluralin	(Parent)
b)	a,a,a Trifluoro-2,6-dinitro p-toluidine (di-dealkalated Trifluralin)	aerobic soil photodegradation
c)	2,6-Dinitro-N-n-propyl-a,a,a-trifluoro-p-toluidine (Mono-dealkylated trifluralin)	aerobic soil photolysis carrot root metabolism
d)	aaa-trifluoro-N',N'-dipropyl toluene-3,4,5 triamine	anaerobic soil rumen fluid
e)	a,a,a-Trifluorotoluene-3,4,5-traimine	anaerobic soil photolysis rumen fluid
f)	a,a,a-Trifluoro-N'-propyltoluene-3,4,5-triamine	anaerobic soil photolysis rumen fluid
g)	aaa-trifluoro-N',N'-dipropyl-5 nitrotoluene-3,4 dimine	anaerobic soil aerobic soil (slight) rumen fluid
h)	a,a,a,-Trifluoro-5-nitrotoluene-3,4-diamine	aerobic soil photolysis (principle acid product) rumen fluid
i)	a,a,a,-Trifluoro-5-nitro-N'-propyltoluene-3,4-diamine	aerobic soil anaerobic soil rumen fluid carrot metabolism
j)	4-(Dipropylamino)-3,5-dinitrobenzoic acid	carrot root
k)	2-ethyl-7-nitro-5 trifluoromethyl benzimidizole	aerobic soil
l)	2-Ethyl-7-nitro-1-propyl-5-trifluoromethylbenzimidazole	aerobic soil photolysis

	Name	Found
m)	2-ethyl-7-nitro-5-trifluoromethyl benzimidazole	aerobic soil photolysis (principal basic pH product)
n)	2,3-dihydroxy-2-ethyl-7-nitro-1-propyl 5-trifluoromethyl-benzimidazoline ~~(VII)~~	intermediate photoproduct
o)	2,3-dihydroxy-2-ethyl-7-nitro-5-trifluoromethylbenzimidazoline	intermediate photoproduct
p)	2-ethyl-7-nitro-5-trifluoro-methylbenzimidazole-3-oxide	intermediate photoproduct
q)	2-ethyl-7-nitro-1-propyl-5-trifluoromethylbenzimidazole-3-oxide	intermediate photoproduct

intermedate photoproducts were detectable in small concentrations after 12 days.

4. Conclusions

4.1 Conclusions presented are a result of an analysis of all of the data presented in this submission; most of the reports analyzed had significant experimental deficiencies. These will be documented in section 5 of this evaluation. Upon presentation of the requested data, the validity of the conclusions presented in this section should be confirmed.

4.2 Data Summary

4.2.1 Soil Metabolism Studies

Aerobic metabolism proceeds through an oxidative dealkylation mechanism that is probably chemical. Soil metabolism half life is about 6 months. On the other hand, anaerobic decomposition involves microbial attack and reduction of the nitrate groups. Under these conditions half life is under ten days. Both mechanisms yield large amounts of bound residues; metabolites never totaled more than 4 percent of applied herbicide.

4.2.2 Photodegradation studies

Photodegradation half-life appears to be short in both vapor and aqueous solution. (Under 36 hours in aqueous dilute solution). The nature of intermediate degradation products is disputed due to decomposition in the GC. The mechanism of degradation involves oxidative dealkylation, nitro reduction and ring formation. Field monitoring of vapor found principally parent compound; this was believed to be an artifact of the short vapor phase residence time before monitoring.

4.2.3 Volatilization Studies

Treflan's volatility is proportional to field moisture and inversely proportional to Cation Exchange Capacity and Organic Matter content.

4.2.4 Herbicide Mobility Studies

Treflan is immobile on loams and clays; it leaches slightly in sand. The herbicide is a member of Helling and Turner's soil TLC class I.

4.2.5 Field Persistence

Hot studies show a half life of parent of 1 to 4 months. Other field studies, referenced but not submitted, determined, the half life to extend for as long as 4 years depending on soil temperatures. After 16 months, 20 to 40% of applied herbicide was detected in the soil as bound residues.

Many cold field studies were presented using bioassay and analytical detection techniques. These techniques gave neither self-consistent results nor results consistent with the general trends from hot studies. Consequently I have not weighed these studies as heavily as the hot studies in my analysis. Cold studies from 107 locations throughout the U.S. showed no significant residue build up after repeated application of herbicide for 1 to 4 years.

4.2.6 Field Leaching Study

Treflan does not leach; it appears that if the soil is tilled, trifluralin returns to the surface (probably through a volatilization mechanism.).

4.2.7 Run-Off Study

The procedure employed does not allow an accurate assessment of run-off; we do not require a run off study.

4.2.8 Plant Metabolism Study

No Trifluralin or major degradation product was found outside the root region in cotton and soybeans. Carrots translocated .49 to .86 ppm ^{14}C as Treflan. Treflan was not found incorporated as a glycosidic conjugate.

4.2.9 Fish Study

Treflan has been shown to accumulate significantly in fish. In a continuous flow dilution experiment with a pesticide concentration of 7.9 ppb, maximum bioconcentration was 12 ppm in edible tissue and 120 ppm in nonedible tissue. This dropped to 7.9 ppm in edible tissue by the start of the withdrawal period. Upon withdrawal this was further reduced to .79 ppm. Testing in nonedible tissue was done only at the point of maximum accumulation.

4.2.10 Effects of Microbes on Treflan

Two rumen microbes degrade Treflan. No loss of CH_4 CO_2 or ring cleavage was noted.

4.2.11 Animal Metabolism Study

Ninety-nine percent of radioactivity ingested by goats was excreted within 6 days; no Treflan was found in the analysis of excreta, no radioactivity was found in blood or milk.

4.2.12 Effect of Treflan on Microorganisms

Actinomycetes count was higher in soil treated with Treflan; bacterial and fungal counts were lower. Rumen ciliated protozoa and bacteria tolerate relatively high concentrations of Treflan. These studies were not done in sufficient detail.

4.3 [A] Persistence

When Treflan is soil incorporated, as required on the label, it is persistent. Apparently this persistence depends on rainfall and temperature, half-lives of 2 months to 4 years have been measured in the field. Under the tested temperature range, bound residues comprised 25 to 50 percent of the total amount of pesticide applied after 1 year. The herbicide accumulates to some extent in carrots; however, little Treflan could be detected in corn or soybeans.

4.4 [B] Rotational Crop

Rotational crop studies on corn and wheat seeds were previously reviewed for double rate Treflan, 7/9/75 (1471-35). Essentially no translocation to the rotational crop was found at these rates. Treflan was found to accumulate in carrots, and no rotational crop data has been presented on root crops. Therefore, this data should be required when the appropriate use patterns are submitted for registration.

4.5 [C] Accumulation

The herbicide concentrates significantly in fish and snails, with an average concentration in water of 7.8 ppb fish accumulation peaked at 12,000 ppb edible, 101,000 ppb nonedible. Upon withdrawal the concentration in edible tissue stabilized at 750 ppb.

The tested concentration in water, 7.8 ppb, represents a level that could reasonably be reached in the environment with a 2 lb a.i./acre application rate, and .5% runoff from the top 6 inches of soil. An experimental field study (Proc. S. Weed Sci. Soc. 26 Meet. 376/1973/, Sheets, Bradley, Jackson) detected a peak of 1.61 ppb of Trifluralin in a pond which received .75 lb a.i./acre herbicide to about 50% of its watershed. Scaling this up to an application rate of 2 lb. a.i./acre on an entire watershed leads one to predict a peak concentration in water of 8.6 ppb. The above article noted that Treflan was detected in runoff from rain 5 to 8 months after application. Since Treflan removal is related directly to amount of rainfall, it is reasonable to expect for larger herbicide buildups in bodies of water when there is more rain in the month immediately following Treflan application than there was in this study.

Based on the above considerations, we may require a simulated field study for additional uses.

4.6 The following submitted studies were not germane to the environmental chemistry assessment 1, 8-10, 25, 31, 33-46.

5.0 Recommendations

5.1 We offer the following comments with this request since it represents no change in the previously accepted pattern of use for Treflan on soybeans and does not fall under section 3 regulation requirements.

5.2 For new uses or amended uses, the following information in support of the submitted studies are needed.

5.2.1 Soil characteristics for references 2, 3, 5, 11, 16, 20, 27-30.

5.2.2 Cultural practices employed must be further described in studies 27-30, 46. In support of study 8 we need to know the cultural operations between cropping.

5.2.3 Rainfall data are needed on References 2, 3, 5, 16, 27-30.

5.3 For further submissions the following additional studies are required.

5.3.1 Hydrolysis

5.3.2 Leaching of major degradation products.

5.3.3 Effect of the pesticide on soil microorganisms.

5.3.4 Referenced but not submitted persistence data

a) Nuland, D.S., B. R. Somerhalder, J. W. Dunse 1970 "The Persistence of Trifluralin in Silt Loam" (abstr.) Proc. N. Cent. Weed Contr. Conf. 25:82-83.

b) Nuland, D.S., J. W. Dunse 1968. "The Persistence of Trifluralin in Soil and its Effects on Milo Yields Two and Four Years after Application" N. Cent. Weed Contr. Conf. Res. Rep't 25:5-6.

5.4 In addition, the following studies may be required, depending on proposed uses if at rates of 2 lbs active and above.

5.4.1 Rotational crop on a root crop. Carrots are the species of choice.

5.4.2 Simulated field run off

The pesticide must be applied at the maximum recommended rate to soil in a field sloping toward a pond containing two or more species of fish including a bottom feeder. Field slope should be 4-6%. Soil, water, bottom sediment and fish must be monitored for residues of the pesticide and degradation products. Fish sampling should monitor residues in non-edible and edible fish fractions. Total residue concentration in the fish must be reported. Residues must be monitored sufficiently often to assess the fate of the pesticide in this environment. Appropriate intervals for residue monitoring would be pretreatment, 1 day, 1 day after first .25" rain or equivalent irrigation, then 1 week, 2 weeks, 1, 2 and 3 months from this data. Tests should be run in two geographic regions.

The ponds used should be large enough to support sufficient fish to allow the sacrificing of at least 3 fish of each species tested at each sampling interval. Rainfall, cultural conditions, and soil characteristics must be reported.

4/22/76

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